PB-230 168

OXIDATION OF SULFUR DIOXIDE IN POLLUTED ATMOSPHERES

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Cincinnati, Ohio

1970

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PB 230 168

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ABSTRACT

Oxidation reactions of sulfur dioxide in polluted atmospheres are discussed. Emphasis is on the photochemical reactions of sulfur dioxide in the wavelength range of 3000 to 4000 A alone and in mixtures with nitrogen oxides and/or hydrocarbons or carbon monoxide. Reactions of sulfur dioxide in the presence of foreign particles on nuclei and reactions of sulfur dioxide with metal salt solutions and droplets are also discussed. The gas-phase reactions, the formation and chemical identity of aerosols, the effect of water vapor, the effect of nucleating particles on photochemical aerosol formation, and the effect of sulfur dioxide on nitrogen oxides - hydrocarbon reaction parameters are included in this review.

Key Words

Oxidation
Photochemistry
Sulfur dioxide
Sulfur trioxide
Sulfuric acid
Atomic oxygen
Ozone
Aerosol
Nuclei
Particulate
Hydrocarbon
Nitrogen oxides
Water vapor
Carbon monoxide
Solution
Droplet

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Introduction

One noticeable physical effect of air pollution is reduced visibility. Visibility in the atmosphere is reduced by the scatter and absorption of radiation by aerosol particles. The quantitative contribution made by the oxides of sulfur to the total scattering of light in various atmospheres has not been resolved, but sulfuric acid mist and other sulfate particulate matter are recognized as important sources of scattering. Sulfate particulates arise from complex oxidation processes, which occur when common atmospheric pollutants interact. The major sulfur pollutant, sulfur dioxide, arises mainly from combustion processes and is oxidized in the atmosphere either photochemically or catalytically.

Two reviews of the photochemical aspects of air pollution have been done by Altshuller and Bufalini (1965) (1970). The earlier review covers the literature through 1963, and the more recent one, from 1963 to the present time. These reviews emphasize the gas-phase photooxidation reactions of hydrocarbon nitrogen oxides systems and only briefly discuss aerosol formation from the irradiation of sulfur dioxide and its mixtures

with hydrocarbons and nitrogen oxides. Urone and Schroeder (1969) surveyed noncritically the photochemical reactions of SO_2. The material presented here constitutes a critical review of the chemical aspects of photochemical and catalytic oxidation of sulfur dioxide and its mixtures with hydrocarbons and nitrogen oxides as related to air pollution. The emphasis is on photochemical reactions of sulfur dioxide, both gas-phase reactions and aerosol-forming reactions. Since there is some interest in the reactions of sulfur dioxide in aqueous metal salt and ammonia solutions due to the relationship of such to fogs, these reactions are also discussed briefly.

For a broader review of air pollution problems, the treatise of Leighton (1961) and the three-volume work edited by Stern (1968) may be consulted.

Photochemical Reactions of SO_2

The photodissociation of SO_2 into SO and O atoms requires 135 kcal per mole and is therefore not possible energetically for wavelengths of absorbed light greater than 2180 A. Since only solar radiation of wavelengths greater than 2900 A reaches the lower atmosphere, the photochemistry of SO_2 within the 3000 to 4000 A range can only involve molecular reactions of the electronically excited states of SO_2.

In the 3000 to 4000 A region, the absorption spectrum of SO_2 shows two bands. The first band is the transition to the first excited state. It originates at 3880 A, with a maximum

around 3840 A, and is a very weak absorption. The second band is the transition to the second excited state. It originates at 3376 A, with a maximum around 2940 A, and is a very strong absorption. The radiative lifetimes suggest that the first excited state is a triplet state ($^3SO_2$) and the second excited state is a singlet state ($^1SO_2$). These states are often referred to as $^3B_1$ and $^1B_1$ states, respectively, and the SO_2 ground state is often referred to as the $^1A_1$ state. The precise roles of the excited singlet and triplet states in the photochemistry of SO_2 are unclear. The primary processes in the photochemistry of SO_2 were described by Rao, Collier, and Calvert (1969a). The primary reactions and the corresponding rate constants are shown in Table 1.

The only observed products from the photolysis of SO_2 alone at 3130 A were SO_3 and S. Hall (1953) reported that the rate of production of SO_3 was proportional to the SO_2 pressure and the quantum yield for the disappearances of SO_2 was about 10^{-2} molecule per quantum absorbed. He postulated that the reaction products arose from the reactions

$$SO_2^* + SO_2 \rightarrow SO + SO_3 \qquad (10)$$

and $$SO \rightarrow SO_3 + S \quad \text{by various steps.} \qquad (11)$$

The asterisk represents an excited SO_2 molecule.

The unspecified product, ($2SO_2$), in reactions 2 and 9 of Table 1 has been discussed by Okuda, et al. (1969). This product can be ground state SO_2, SO_3, and SO, and/or possibly some other chemical products that do not regenerate any excited

state of SO_2. The photochemical formation of SO_3 from SO_2 is suggested by experimental evidence, but there is no requirement that SO_3 is indeed the oxidation product. There has been no direct spectroscopic evidence for SO_3 formation in this system. Okuda et al. (1969) state that, conceivably, the primary product may be a metastable dimer of SO_2 (O_2S-O-S-O) or even the reactive tetroxide of sulfur (SO_4). However, their results at present favor the following more detailed description of reaction 9

$$^3SO_2 + SO_2 \rightarrow SO_3 + SO(^3\Sigma^-) \qquad 9a$$

Photochemical Reactions of SO_2-O_2 System

Studies of the fluorescence and phosphoresence of SO_2 suggest that the reactivities of the triplet and singlet states of SO_2 are quite different. This was confirmed by the work of Rao, Collier, and Calvert (1969b) on quenching reactions of the two states with oxygen. Based on the mechanistic reaction steps 1 through 9 plus the following steps

$$^1SO_2 + O_2 \rightarrow (SO_2\text{-}O_2) \qquad (12)$$

$$^1SO_2 + O_2 \rightarrow {}^3SO_2 + O_2\ (^3\Sigma,\ ^1\Delta,\ ^1\Sigma) \qquad (13)$$

$$^3SO_2 + O_2 \rightarrow (SO_2\text{-}O_2) \qquad (14)$$

they deduced that $k_2 + k_3 = 1.5 \pm 0.7 \times 10^{10}$ ℓ mole^{-1} sec^{-1}, $k_{12} + k_{13} = 0.47 \pm 0.22 \times 10^{10}$ ℓ mole^{-1} sec^{-1}, $k_9 = 1.4 \pm 0.7 \times 10^7$ and $k_{14} = 1.1 \pm 0.6 \times 10^7$ ℓ mole^{-1} sec^{-1}. The values for $k_2 + k_3$ and k_9 agree within experimental error with their

previous work. The formation of O_2 in the $^1\Delta$ or $^1\Sigma$ state in reaction 13 is energetically possible only if the $^1SO_2$ is in a vibrationally nonequilibrated excited singlet state. The rate constant for the quenching of $^1SO_2$ with O_2 is near the collision number, whereas the quenching rate for $^3SO_2$ is much lower. In fact, it is the lowest reported value for a triplet molecule quenching reaction by oxygen. It is suggested that the slowness of energy transfer to oxygen from $^3SO_2$ forming $^1\Delta$ or $^1\Sigma$ states of oxygen is related to the relative unimportance of charge-transfer states in the O_2-$^3SO_2$ collision complex.

An early study of the photochemistry of SO_2-O_2 mixtures was reported by Blacet and Hall (Blacet, 1950). They obtained a quantum yield of 10^{-3} for the decomposition of SO_2 at 3130 A. Blacet (1952) later reported that when the O_2 concentration is high in comparison to SO_2, ozone and SO_3 appear to be the only products. The secondary reaction steps in the photooxidation of SO_2 were described as

$$SO_2^* + O_2 \rightarrow SO_4 \qquad (15)$$

$$SO_4 + O_2 \rightarrow SO_3 + O_3 \qquad (16)$$

and in the presence of water

$$H_2O + SO_3 \rightarrow H_2SO_4 \qquad (17)$$

The quantum yield for sulfate production was 10^{-2} to 10^{-3} molecule per quantum absorbed. Blacet (1959) later supplemented the above mechanism by adding the reaction

$$SO_4 + SO_2 \rightarrow 2SO_3 \qquad (18)$$

Blacet's publications, however, do not present the data for these studies and since there is no proof that ozone is indeed formed, this mechanism can only be viewed as speculative.

Gerhard and Johnstone (1955) studied the photooxidation of SO_2 at concentrations of 5 to 30 ppm and 32 to 91 % relative humidity under static conditions. The irradiations were carried out in a 7.94 ℓ Lucite cell with a General Electric type RS, 275 watt sunlamp (3650 - 2950 A). The rate of decomposition of SO_2 was determined by measuring the formation of H_2SO_4. The H_2SO_4 aerosols were analyzed by impacting the particles upon an acid-base indicator film. The rate of formation of H_2SO_4 was found to be first-order with respect to SO_2 and was 0.68 % per hour. It is difficult to convert this rate into an exact quantum yield, since the authors' only statement concerning intensity of the ultraviolet source is that "the intensity of the ultraviolet in the region from 2950 to 3200 A in the sunlamp chamber was approximately three times as great as the noon sunlight on a clear day and approximately five times as great as in the natural sunlight reaction chamber." This does not necessarily mean the reaction with the GE lamp is 3 times faster than the photooxidation rate in natural sunlight. With the 64 cubic foot reaction cell, their irradiations in natural sunlight indicated the rate of formation of H_2SO_4 to be approximately 0.1 % per hour. Hall's (1953) studies under natural sunlight between 10 a.m. and 3 p.m., with 56 to 230 mm SO_2 mixed with 50 to 200 mm O_2 indicated that the rate

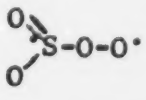
of formation of SO_3 was first-order with respect to SO_2, was independent of the concentration of oxygen, and was about 0.05 % per hour.

Renzetti and Doyle (1960), while studying the photochemical formation of aerosol in sulfur dioxide - hydrocarbon systems, did some irradiations in which only SO_2 in air (0.2 to 0.6 ppm) and water vapor were present. The irradiations were carried out in a 50-ℓ Pyrex stirred-flow reaction flask, with four General Electric H 400-E1 medium pressure mercury arc lamps. The intensity within the reactor of these lamps in the 3000 to 4000 A region was about 10^{15} quanta sec^{-1} cm^{-1}. The SO_2 was measured colorimetrically. They obtained a quantum yield for the disappearance of SO_2 of about 0.3 molecule per quantum absorbed. However, when the concentration of SO_2 was increased to 12.7 mm and the O_2 concentration was 10.6 mm and no water vapor was present, the quantum yield for the disappearance of SO_2 decreased to 0.036 molecule per quantum absorbed. Their data do not indicate whether this decrease was due to the lack of H_2O or to the higher concentrations of SO_2 and O_2. From their light scattering data they calculated that the complete conversion of 0.05 ppm SO_2 to aerosol of 50 % relative humidity will result in a mass loading of about 460 $\mu g/m^3$ of a 43 % solution of H_2SO_4. A mass loading of this magnitude will significantly reduce visibility.

Renzetti and Doyle (1960) suggest that the absorption of a photon by SO_2 promotes it to a highly excited vibrational

state of the second electronic level ($^1SO_2^v$) and that this vibrational state can be identified with the reactive species of reactions 10 and 15. They consider that the first electronic state of SO_2 ($^3SO_2$) is a biradical having an unpaired electron in a sulfur sp^3 orbital, and thus reaction 15 is facilitated. Walsh's (1953) molecular orbital calculations indicate that the first excited electronic state of SO_2 is a "bent" state, having a different O-S-O bond angle then the ground electronic state. The experimental findings of Renzetti and Doyle (1960) impose the condition that the rate of reaction 15 be much more rapid than the rate of deactivation of SO_2^* at oxygen pressures greater than about 50 mm. Thus, they concluded that this "bent" state is sufficiently stable with regard to collisional deactivation that it reacts almost completely with oxygen at relatively high oxygen partial pressures and at total pressures ranging from 0.1 to 1 atmosphere.

Leighton (1961) suggested that the SO_4 molecule formed would have a peroxy structure, and if SO_2^* is a triplet the SO_4 molecule might also be a biradical



More recently Urone, Lutsep et al. (1968) irradiated SO_2 (12 and 19 ppm) tagged with $S^{35}O_2$ in air (50 % relative humidity) in a 2-ℓ flask. Their photochemical chamber contained a bank of 16 intermediate pressure ultraviolet lamps (3100 - 4200 A).

The intensity of the lamps as measured by potassium ferrioxalate actinometry was 5.4×10^{15} photons sec^{-1} cm^{-2}. Their analysis of the system was designed to account for the total amount of SO_2 initally present. The unreacted SO_2 was measured colorimetrically (West-Gaeke Method) and a scintillation method was used to account for all the SO_2 taken. The rate of disappearance of SO_2 was approximately 0.6 % per hour. It is unfortunate that they choose to express this rate as 0.1 % per hour of noonday sunlight rather than the more meaningful quantum yield since they had measured the intensity of their lamps. They could account for 99.5 to 98 % of the sulfur.

Sethi, Allen, and Cadle (1968) determined quantitatively the quantum yields for the disappearance of SO_2 (Φ_{SO_2}) using a photometric method to monitor SO_2 concentration. The dependence of Φ_{SO_2} on the initial SO_2 (20-100 Torr) and initial oxygen (50-390 Torr) pressures were studied at room temperature. Over an 8 hour photolysis with an intense ultraviolet light source (10^{18} quanta sec^{-1}), conversions of about 10 % were observed. Φ_{SO_2} at 3130 A was 1.7×10^{-2} molecule per quantum absorbed and over the integrated wavelength range 2800 to 4200 A, it was 2×10^{-3} molecule per quantum absorbed. In both cases Φ_{SO_2} was essentially independent of the initial oxygen and sulfur dioxide concentrations. Also, addition of inert gases, such as N_2 and CO_2, had no observed effect on Φ_{SO_2}.

In contrast with these findings are results obtained by Billings et al. (1968) for the photooxidation of 3130 A of SO_2 in oxygen at concentrations from 60 to 100 % SO_2. For pure SO_2, the quantum yield for SO_3 formation was 0.05 molecule per quantum absorbed. As O_2 was added to the system, the quantum yield increased to a value of 0.22 molecule per quantum absorbed for a 60:40 SO_2-O_2 mixture. They explain their results with a mechanism involving formation of an oxygen atom from the reaction of excited SO_2 with O_2.

$$SO_2 + h\nu \rightarrow SO_2^*$$

$$SO_2^* + SO_2 \rightarrow 2SO_2 \quad (19)$$

$$SO_2^* + SO_2 \rightarrow SO_3 + SO \quad (20)$$

$$SO_2^* + O_2 \rightarrow SO_3 + O \quad (21)$$

$$SO_2 + O \rightarrow SO_3 \quad (22)$$

$$O + O_2 \rightarrow O_3 \quad (23)$$

$$SO + O_2 \rightarrow SO_3 \quad (24)$$

$$SO + \text{Wall} \rightarrow SO \text{ lost} \quad (25)$$

According to this mechanism, SO_3 formation occurs only by reaction 20 in pure SO_2 and the low quantum yield is due to the effectiveness of ground state SO_2 deactivating excited SO_2.

Reactions 21, 22, and possibly 24 account for the initial increase in quantum yield as oxygen is added. As the oxygen is further increased, the predominant steps become reactions 21 followed by 22. At lower SO_2 concentrations ϕ_{SO_3} would be

expected to decrease as a consequence of the competition for oxygen atoms caused by ozone. Although not included, the deactivation of excited SO_2 by O_2 would also be important.

Another point not discussed by the authors is the formation of O_3 in reaction 23. Although the rate constant for the oxygen atom-O_2 reaction is an order of magnitude less than that for the oxygen atom-SO_2 reaction, the rate of formation of O_3 in reaction 24 will be 10^4 to 10^5 times greater than the rate of formation of SO_3 in reaction 22. Thus, if it is assumed that at atmospheric concentration levels reactions 22 and 25 are unimportant and if k_{20} and $k_{21} = 10^7$ or 10^{10} ℓ mole^{-1} sec^{-1}, depending on whether SO_2 is in the singlet or triplet excited state (Rao, Collier and Calvert, 1969), and $(O_2) = 10^5$ to $10^6(SO_2)$ then the steady-state kinetic expression predicts that the rate of O_3 formation would be approximately the same as the rate of SO_3 formation. Unfortunately, no effort was made to substantiate this mechanism by a check for ozone.

Since SO_3 is a known product of the photooxidation of SO_2 in the 3000 to 4000 A range, consideration must be given to the photochemistry of this product. Little work has been done on the photochemistry of SO_3, but some earlier work (Fajans and Goodeve, 1936) shows that absorption does occur in the ultraviolet region with weak diffuse bands superimposed on a continuum extending to about 3100 A. From energy considerations the following photodecompositions

$$SO_3 + h\nu \rightarrow SO_2 + O\ (^3P) \quad (26)$$

$$SO_3 + h\nu \rightarrow SO + O_2\ (^3\Sigma) \quad (27)$$

may occur at 3440 A and 3000 A, respectively.

In the presence of O_2, reaction 26 would cause a competition between O_2 and SO_2 for the oxygen atom, with subsequent formation of ozone and SO_3. It would be expected that formation of ozone would predominate because of the high concentration of O_2. A decrease in Φ_{SO_3} would occur to the degree that the photodecomposition of SO_3 occurs.

The SO formed in reaction 27 would probably react either with O_2 to form SO_3 or with SO_2 to form S and SO_3, the former process predominating. In any event, the end product would still be SO_3, and no net effect on Φ_{SO_3} would likely occur. If both photodecomposition precesses were occurring, the net effect would be dependent on the value of the primary quantum yield for the two processes.

In summary, the reason for such a large discrepancy in the reported quantum yields for the disappearance of SO_2 is not readily apparent. The reported values vary from 10^{-3} to 10^{-1} molecule per quantum absorbed. The mechanism is highly speculative. There is no direct evidence for formation of an SO_4 intermediate nor for formation of ozone.

Photochemical Reactions of SO_2-NO_x System

Gerhard and Johnstone (1955) carried out a series of experiments in which 1 to 2 ppm of NO_2 were added to 10 to 20 ppm SO_2 and irradiated with light in the range of 2950 to 3650 A.

No measurable effect on the rate of H_2SO_4 production was observed, and no dark reaction between SO_2 and NO_2 occurred.

In contrast to that work, Renzetti and Doyle's (1960) experiments indicated that the addition of 1 ppm NO_2 to 0.14 ppm SO_2 enhanced the photooxidation of SO_2 (as measured by a light-scattering photometer), whereas the addition of 1 ppm NO to 0.5 ppm SO_2 at a relative humidity of 50 % hindered the formation of aerosol. They account for the enhancement of the rate by NO_2 with the reaction

$$SO_2 + O + M \rightarrow SO_3 + M \qquad (28)$$

and suggest that the reaction

$$SO_4 + NO \rightarrow SO_3 + NO_2 \qquad (29)$$

can account for the suppressing effect of NO. As Altshuller and Bufalini (1965) have pointed out, this explanation for the decrease due to NO is not very appealing because the end product of the reaction is still SO_3. If, however, more SO_3 is formed by reaction 18 than by reaction 16, then the net result of reaction 29 would be a decrease in SO_3. With excess O_2, though, it is unlikely that reaction 18 will predominate. Altshuller and Bufalini (1965) suggest that the removal of SO_3 or the deactivation of excited SO_2 with NO is a more plausible explanation.

Adding to the confusion are results reported by Ripperton, Decker and Page (1962), who irradiated mixtures of SO_2 (1 ppm) and NO_2 (1 ppm) at a relative humidity of 44 % in a nylon bag using 30 watt daylight fluorescent lamps, plus two 400 watt mercury vapor lamps. These experiments showed very little SO_2

destruction in comparison with an SO_2 consumption rate of 30 % in 4 hours when SO_2 was irradiated in the absence of NO_2. Their results indicate that NO_2 interferes with SO_2 destruction, at least when the ratio of the two gases is 1 to 1. They interpret the slower rate of SO_2 disappearance in the NO_2-SO_2 system as an indication that SO_2 is not being rapidly oxidized by atomic oxygen produced from the photolysis of NO_2.

Thus, addition of NO_x to low concentrations of SO_2 seems to produce varying results. To discuss the reactions that occur when mixtures of SO_2 and NO_x are photolyzed in the presence of O_2, the primary reactions of NO and NO_2 when exposed to 3000 to 4000 A radiation must first be considered. The electronic absorption spectrum of NO starts just below 2300 A and extends well into the vacuum ultraviolet region; thus, in the region of 3000 to 4000 A there is no photodissociation of NO or formation of electronically excited NO molecules.

The thermal oxidation of NO by molecular O_2

$$2NO + O_2 \rightarrow 2NO_2 \qquad (30)$$

is slow ($k_{30}^{20^oC} = 10.0 \times 10^3\ \ell^2 mole^{-2}\ sec^{-1}$ (Greig and Hall, 1966)), but it is important because the thermal oxidation product, NO_2, upon photolysis serves as a source of oxygen atoms. In model systems, even though extreme caution is taken to remove all of the NO_2 originally present in the NO, enough NO_2 is formed to initiate reactions between oxygen atoms and other components present.

NO_2 absorbs over most of the visible and utraviolet spectrum. All of the evidence (Pitts et al., 1963; Sato and Cvetanovic, 1958; Noyes and Leighton, 1941) indicates that the photodissociation of NO_2 occurs at wavelengths shorter than 4047 A by the process

$$NO_2 + h\nu \rightarrow NO\ (X^2\pi) + O\ (^3P) \qquad (31)$$

When NO_2 is present in low concentrations in air, the oxygen atom will react with O_2 to produce O_3, which in turn reacts with NO produced in the initial photodissociation to produce NO_2 and O_2. The net result will be a steady state in which small concentrations of O_3 and NO are present.

Bufalini and Stephens (1965) described the mechanism for the thermal oxidation of NO in the presence of ultraviolet light as

$$2NO + O_2 \rightarrow 2NO_2 \qquad (32)$$

$$NO_2 + h\nu \rightarrow NO + O \qquad (33)$$

$$O + NO_2 + M \rightarrow NO_3 + M \qquad (34)$$

$$O + NO_2 \rightarrow NO + O_2 \qquad (35)$$

$$O + NO + M \rightarrow NO_2 + M \qquad (36)$$

$$NO_3 + NO \rightarrow 2NO_3 \qquad (37)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (38)$$

$$O_3 + NO \rightarrow O_2 + NO_2 \qquad (39)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (40)$$

Thus, when SO_2 is photolyzed in the presence of NO_x the following reactions should be considered. These reactions can be classified as dark reactions of the reactants, oxygen atom

reactions, ozone reactions, and other reactive intermediate reactions.

$SO_2 + NO$	→	$SO + NO_2$		(41)
$SO_2 + NO_2$	→	$SO_3 + NO$		(42)
$SO_2 + O + M$	→	$SO_3 + M$		(43)
$SO_2 + O_3$	→	$SO_3 + O_2$		(44)
$SO_3 + C$	→	$SO_2 + O_2$		(45)
$SO_4 + NO$	→	$SO_3 + NO_2$		(46)
$SO_4 + NO_2$	→	$SO_3 + NO_3$		(47)
$SO_4 + O$	→	$SO_3 + O_2$		(48)
$SO + O$	→	SO_2		(49)
$SO + O_3$	→	$SO_2 + O_2$		(50)
$SO + NO_2$	→	$SO_2 + NO$		(51)

Jaffee and Klein (1966) report for reaction 42 a specific rate constant of 3.7×10^{-3} ℓ mole^{-1} sec^{-1} in the dark, both components at high concentration and no O_2 present. Thus, reaction 42 would not be an important reaction in the SO_2-NO_x system. From all indications SO_2 in the presence of O_2 does not react with NO and NO_2 in the dark. If a reaction occurs, the rate constants must be extremely small.

There will be competition for the oxygen atom that is formed in the photodissociation of NO_2 by O_2, NO_2, and SO_2. The bimolecular oxygen atom-SO_3 reaction (reaction 45) does not take place at room temperature (Kaufman, 1961). Although the rate constant for the oxygen atom-O_2 reaction is two to

three orders of magnitude less than that for reaction of the oxygen atom with NO_2, NO, or SO_2, the oxygen atom-O_2 reaction will be the most effective in removing oxygen atoms since the concentration of O_2 is 10^5 to 10^6 times greater than that of the other components. However, depending upon the ratio of concentrations of NO or NO_2 to SO_2, it is possible that SO_2 could be an effective secondary competitor, at least with NO or NO_2, for the oxygen atom. By a consideration of the magnitude of the rate constants[1]. k_{34}, k_{35}, k_{36}, k_{43}, the effectiveness of oxygen atom-SO_2 reaction increases as the SO_2/NO_x concentration ratio increases.

When the SO_2/NO_x ratio is high, the SO_2 reaction will be of greater importance. At extremely low SO_2/NO_x ratios, the SO_2 reaction would be of minor importance. Evidence for this is found in the work of Jaffee and Klein (1966). They report that with 3×10^{-4} mole ℓ^{-1} of NO_2 and up to 4×10^{-2} mole ℓ^{-1} of SO_2 the quantum yield for the disappearance of NO_2 decreases as SO_2 increases, an indication that SO_2 is indeed effectively competing with NO_x for the oxygen atom. In photochemical smog, concentrations of 20 pphm of NO_x and 20 pphm of SO_2 are typical.

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1. $k_{34} = 4.2 \times 10^{10}$ ℓ^2 mole^{-2} sec^{-1} and $k_{35} = 5.3 \times 10^9$ ℓ mole^{-1} sec^{-1} and $k_{36} = 2.3 \times 10^{10}$ ℓ^2 mole^{-2} sec^{-1} (Schuck, Stephens and Schrock, 1966). $k_{43} = 2.7 \times 10^9$ ℓ^2 mole^{-2} sec^{-1} (Mulcahy, Steven, and Ward, 1967).

At a SO_2/NO_x ratio of about 1, SO_2 can compete favorably with NO_x for oxygen atoms. However, the contradictory results obtained for SO_2-NO_x-air systems cannot be explained by differences in the SO_2/NO_x ratio; they may be due to differences in the design of the experimental equipment.

Ozone may react with NO, NO_2, or SO_2. The work of Stanford Research Institute (Jacobs, 1960) indicates that the SO_2-O_3 reaction cannot be important. They reacted 1 to 10 % SO_2 with 1 % O_3 (an extremely high value of O_3 as far as air concentrations are concerned) and 1 % water vapor and found that less than 0.1 % of the SO_2 had reacted in a 24-hour period. Further confirmation is the work of Dunham (1960), which indicates that very few, if any, condensation nuclei of H_2SO_4 are formed from the SO_2-O_3 reaction. The rate constants[2.], k_{39} and k_{40}, for the reaction of O_3 with NO_2 or NO signify the importance of the O_3-NO_2 reaction in the SO_2-NO_x photochemical system.

Very little is known about the reactions of SO_4 and SO. As a matter of fact, there is no evidence for the existence of SO_4. Some work is available on the reactions of SO with oxygen atoms (Rolfes et al., 1965; Sharma et al., 1967;

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2. $k_{39} = 2.8 \times 10^7$ ℓ mole^{-1} sec^{-1} (Ford, Doyle, and Endow, 1957).
   $k_{40} = 4.3 \times 10^4$ ℓ mole^{-1} sec^{-1} (Johnston and Yost, 1949).

Halstead and Thrush, 1964; Halstead and Thrush, 1966) and with NO_2 (Clyne et al., 1966).

Thus, for the reaction of SO_2 in the presence of NO_x in O_2, all likely reactions that can be postulated except for the reactions of SO with oxygen atoms, ozone or NO_2 and the atomic oxygen - SO_3 reaction will lead to enhancement of the formation of SO_3. If indeed the disappearance of SO_2 is retarded in the presence of NO, more than likely this would be caused by the effective deactivation of electronically excited SO_2 molecules by NO. More work is needed on this reaction system before a quantitative assessment can be given. The effect of the SO_2/NO_x ratio over a wide range of concentrations should be ascertained; rate constants for SO_2 reactions, and more information on aerosol formation are needed.

Photochemical Reactions of SO_2-Hydrocarbon System

A. Paraffins

Dainton and Ivin (1950) reported results of the gas-phase reactions of paraffinic hydrocarbons with SO_2 at high concentrations in the absence of O_2. A mercury vapor lamp emitting wavelengths greater than 2300 A was used as an ultraviolet source. The reaction was followed by measuring the pressure fall, and the unreacted SO_2 was measured by titration. The reaction of SO_2 with methane, ethane, propane, n-butane, isobutane, and n-pentane was investigated.

The investigators observed a pressure fall and formation of a mist, which on settling gave a colorless or pale yellow involatile oil with a disagreeable odor. Molecular weight determinations, and infrared and elemental analyses of the solid product from the n-butane - SO_2 reaction indicated the presence of $C_4H_{10}SO_2$ (sulfinic acid) mixed with some disulfinic and disulfonic acids. For the normal paraffins the quantum yield increased as the number of carbon atoms increased. The quantum yield for the branched-chain isobutane was between the values for n-propane and n-butane.

Kinetic data for the n-butane - SO_2 reaction show that the rate of disappearance of SO_2 is first-order with respect to light intensity and is fractional-order with respect to n-butane for n-butane pressures less than 200 mm. Butadiene and 1-butene retarded the reaction markedly. Dainton and Ivin (1950) postulated a mechanism involving the initial formation of a biradical,

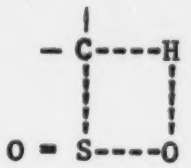
$$\begin{array}{ll} R & O \\ \cdot CH - CH_2 - & C\cdot \\ R & O \end{array}$$

and the sulphinic acids were formed by enolization reactions.

Timmons (1969) irradiated a fixed pressure of SO_2 and varying amounts of n-butane, isobutane, propane, ethane, or methane at 3130 A. The decrease in pressure, plus mass spectrometric and gas chromatographic analysis indicated a

stoichiometric ratio of one SO_2 molecule removed per molecule of hydrocarbon reacted when the concentration of SO_2 was much lower than the concentration of hydrocarbon. When the concentration of SO_2 was equal to or greater than the concentration of hydrocarbon, the ratio of SO_2 consumed to hydrocarbon consumed always exceed unity. The quantum yields for hydrocarbon consumption were pressure dependent, ranging from 0.07 for isobutane to less than 0.01 for methane for equal initial concentrations of SO_2 and hydrocarbon. Sulfur-containing products, such as sulfinic acids were observed but no oxygen-containing organic products were found. Only small amounts of other hydrocarbons were present. Timmons concluded that the interaction between excited SO_2 and hydrocarbon does not proceed via a free radical mechanism, since no hydrocarbon cracking was observed. However, Ogato, Izawa, and Tsuda (1965) earlier postulated a free radical mechanism for the photochemical reaction of SO_2 with n-hexane, which involves the simultaneous formation of alkyl radicals by reaction of the paraffin with excited singlet SO_2 and energy transfer by the excited SO_2 molecule. The singlet-triplet energy separation of SO_2 is approximately 13 kcal per mole, and since the paraffinic hydrocarbon C-H bond dissociation energy is of the order of 100 kcal per mole it is highly doubtful whether energy transfer by the excited singlet, forming SO_2 in the triplet state, could supply the necessary energy for alkyl radical formation. Of interest is the suggestion by Trotman-Dickenson (1955) that the reactions

are probably molecular, involving a four center activated complex.



Johnston and dev Jain (1960) irradiated mixtures containing 20 and 50 mm each of SO_2 and n-butane in the presence of dry air with natural sunlight as the ultraviolet source. The formation of aerosol was light when SO_2 and n-butane only were present at 20 mm pressure each but became heavy when air was also present. The liquid product was colorless when only SO_2 and n-butane were present but was light yellow when air was also present. When SO_2 and n-butane were increased to 50 mm, the formation of aerosol was heavy within 2 minutes after the mixtures were placed in sunlight. Qualitative chemical tests indicated that the liquid product was a mixture of highly oxidized strong organic acids containing sulfur. These results led the authors to propose that the photochemical reactions of SO_2 with paraffinic hydrocarbons were important in air pollution because of the formation of aerosols.

More recently Kopczynski and Altshuller (1962) investigated the photochemical reactions of paraffinic hydrocarbons with SO_2 using lower concentrations (50 to 1000 ppm). The reactions of n-butane, isobutane, and neopentane with SO_2 were studied in irradiations with either a mercury sunlamp or a mercury arc. Infrared spectra of the gaseous components were obtained before and after each irradiation. Formation of

aerosol or liquid film was determined visually.

When high concentrations (12 mm each) of SO_2 and hydrocarbon were irradiated with either the sunlamp or mercury arc, appreciable quantitites of condensate formed on the walls and a strong band at 5.7 microns, attributed to carbonyl, was present. This confirmed Johnston and dev Jain's work at high concentrations. However, when the concentrations were decreased to 1 mm each, only a light condensate and a weak carbonyl band were present with the mercury arc and no detectable condensate or carbonyl was present with the sunlamp.

At concentrations in the 0.05 to 0.10 mm range, no film could be detected with either the mercury arc or sumlamp. The investigators concluded that reactions of SO_2 with saturated hydrocarbons do not contribute significantly to the formation of aerosols in air pollution situations.

B. Olefins

Dainton and Ivin (1950) found that irradiation of high concentrations of SO_2 and 1-butene produced an oil which, upon further irradiation, formed a solid that resembled a polysulphone. Renzetti and Doyle's (1960) experiments in which butadiene or 1-pentene (3 ppm) was added to SO_2 (0.3 ppm) and irradiated with a medium pressure mercury arc indicated that production of aerosol was suppressed by the olefins. Kopczynski and Altshuller (1962) found no detectable condensate in the presence of SO_2 at corresponding concentrations.

Thus, all the available evidence indicates that the reactions of SO_2 in the presence of hydrocarbons at levels that occur in a polluted atmosphere are not significant in the formation of aerosols. It would seem that if O_3 is indeed formed as postulated in the photooxidation of SO_2, its presence would be manifest by the formation of aldehydes and ketones, which are major products observed from gaseous olefin-ozone reactions.

Photochemical Reactions of the SO_2-NO_x-Hydrocarbon System

Prager et al. (1960) surveyed the formation of aerosols from different types of hydrocarbons mixed with NO_2 in the presence and absence of SO_2. The reactions were carried out in a long path infrared cell with radiation greater than 3000 A (General Electric AH-6 mercury lamp). The aerosols were measured with a smoke photometer, and the rate of disappearance of NO_2 was measured by scanning the 6.1 μ band of NO_2. Results are summarized in Tables 2, 3, and 4. Paraffinic hydrocarbons (n-butane and 2-methylpentane) gave little or no aerosol in the presence of NO_2 and SO_2. Mono-olefins (ethylene, 1-butane, 2-butene, 1-pentene, 2-pentene, 1-hexene, 2-hexene, and 3-heptene) produced no appreciable amounts of particulates in the presence of only NO_2 but produced large quantities of aerosols when SO_2 was added to the hydrocarbon-NO_2 blend. The amount of aerosol produced increased as the number of carbon atoms in the mono-olefin increased. Whereas, very little

particulate was produced during irradiation of straight-chain mono-olefins and NO_2 aerosol formed slowly in irradiations of diolefins (1,3-butadiene and 1,5-hexadiene) and NO_2. The 1,5-hexadiene - NO_2 system produced a significantly larger number of aerosols than the 1,3-butadiene. In the presence of SO_2 and NO_2, the increase in aerosol was larger for the butadiene than for the hexadiene; the reading for the butadiene-NO_2-SO_2 system was somewhat lower than the reading for the hexadiene-NO_2 system.

Little information is available on the acetylenic hydrocarbons. The work of Renzetti and Doyle (1960) indicates that 1-butyne forms no aerosol when irradiated in the presence of NO and forms only a very small amount, if any, in the presence of NO and SO_2.

Irradiation of cyclic saturated hydrocarbons (cyclopropane and cyclohexane) in the presence of NO_2 produced little or no aerosol, whereas irradiation of cyclic olefins (cyclopentene, cyclohexene, and dicyclopentadiene) in the presence of NO_2 gave a large amount of aerosol whether SO_2 was present or not. The rate of aerosol production with cyclic olefins was much more rapid than the rate with straight-chain olefins; SO_2 did not significantly affect the rate of aerosol production or the amount of aerosol obtained (Prager et al., 1960).

Data on aerosol formation in aromatic systems are meager. Early work by Renzetti and Doyle (1960) indicated that aromatics

(benzene, toluene, ethyl benzene, and p-xylene) in the presence of NO alone formed no aerosol. These aromatic compounds in the presence of both NO and SO_2 formed significantly less aerosol than did the olefin - NO-SO_2 systems. The more recent work of Altshuller et al., (1966) and the Air Pollution Control District, County of Los Angeles (1966) disagrees with the work of Renzetti and Doyle. Aerosol formation in the toluene - NO system and trimethyl benzene - NO system occurs to an extent comparable with formation in the ethylene - NO_2-SO_2 system. Benzene and xylene in the presence of both NO_x and SO_2 form little aerosol whereas toluene in the presence of NO and SO_2 forms aerosol to an extent comparable with formation in olefin - NO-SO_2 systems. A 1-to-1 mixture of toluene and xylene (NO_x and SO_2 present) produces a significantly greater quantity of aerosol than that found from the single aromatic compound. Under the proper conditions the toluene - xylene mixture forms aerosol in excess of that formed from irradiated auto exhaust. Apparently a large aerosol synergistic effect occurs in aromatic hydrocarbon - NO_x-SO_2 systems. A detailed investigation of aerosol formation from aromatic systems is needed.

Of interest here are the experiments of Stevenson et al. (1965), in which trans-2-butene was added to the cyclohexene-NO_2 system after aerosol was formed. Concentrations of trans-2-butene greater than 3 ppm caused a marked decrease in aerosol, whereas concentrations of 3 ppm or less increased the aerosol.

Unfortunately no co-hydrocarbon irradiations were made in the present of both SO_2 and NO_2.

The reactions taking place when NO_x is irradiated in the presence of hydrocarbons are summarized briefly in the following paragraphs. The summary is followed by discussion of the effect of mixtures of hydrocarbon and NO_x on the rate of disappearance of SO_2, the effect of SO_2 on the rate of consumption of hydrocarbon and rate of oxidant formation, and the effect of the ratio of reactants in the SO_2-NO_x-hydrocarbon system.

When hydrocarbons are present with NO and ultraviolet light, the equilibrium

$$NO_2 + O_2 \overset{h\nu}{\rightleftarrows} NO + O_3 \qquad (52)$$

is disrupted. The NO is oxidized almost completely to NO_2 and ozone builds up with the disappearance of NO. The ozone does not appear until NO_2 is at its maximum value and a subsequent increase in O_3 occurs as NO_2 then decreases. A typical profile of the olefin-NO_2 reaction is shown in Figure 1 (Altshuller and Cohen, 1963). The major products in the photooxidation of hydrocarbons in the presence of NO include ozone (or oxidant), aldehydes, ketones, carbon monoxide, and organic nitrates. Small yields of epoxides, alcohols, esters, and peroxides have been obtained in some systems. Most of the products can be explained by an initial attack by either atomic oxygen or ozone, which produces hydrocarbon radicals, alkoxy radicals, and hydroperoxy radicals. Further fragmentations,

rearrangements, and reactions of the radicals with other substituents produce the observed products.

Rate constants for the ozone-hydrocarbon reactions are generally lower than those for atomic oxygen - hydrocarbon reactions by a factor of 10^4 to 10^5. However, since ozone is present at a much higher concentration than atomic oxygen, it still is an important reactant for hydrocarbons. The available rate constant data show that the rate constants for the reactions of ozone with olefins are one to three orders of magnitude larger than those obtained for reactions of ozone with paraffinic hydrocarbons, acetylene, and aromatic hydrocarbons. Likewise, the atomic oxygen - olefin rate constants are larger than those obtained for the reaction of atomic oxygen with paraffinic hydrocarbons and aromatic hydrocarbons. For more detailed discussions of hydrocarbon-NO_x reactions, the reviews of Altshuller and Bufalini (1965, 1970) may be consulted.

Although Renzetti and Doyle's (1960) measurements of SO_2 concentration are uncertain because of difficulty in measuring such low concentrations with their apparatus, consideration of all their data for different classes of hydrocarbons indicates a marked increase in the disappearance of SO_2 in the presence of hydrocarbons and NO over that observed in irradiation of SO_2-O_2 mixture. It is impossible to ascertain the amount of increase with type of hydrocarbon because the SO_2 concentration measurements are so uncertain. However, a series of experiments

on the photooxidation of 2-methyl-2-butene in the presence of NO and SO_2 indicates that the increase in SO_2 disappearance is dependent upon the ratio of reactants. When initial concentrations of SO_2 and NO are held constant at 0.1 and 1 ppm, respectively, and the olefin concentration is decreased from 3 ppm to 0.5 ppm, the rate of disappearance of SO_2 increases. The rate also increases if the olefin and NO concentrations are held constant at 3 ppm and 1 ppm, respectively, and the SO_2 concentration is decreased from 1 to 0.1 ppm. These results indicate that low concentrations of olefin can be quite effective in photooxidizing SO_2 in the presence of NO.

The effect of the ratio of reactants on the formation of aerosol was pointed out by Harkins and Nicksic (1965b). They found that light scattering was directly proportional to the concentration of SO_2 (0 to 16 ppm) when the concentration of propylene was 5 ppm and concentration of NO_2 was 2 ppm. These findings seem to contradict those of Renzetti and Doyle (1960), who observed that at 3 ppm olefin and 1 ppm NO, the rate of SO_2 consumption increased as SO_2 concentration was decreased from 1 to 0.1 ppm. This implies that the formation of aerosol is proportional to the initial concentration of SO_2 but is not proportional to the rate of disappearance of SO_2. With the ratio of propylene to NO to SO_2 held constant at 5 to 2 to 0.5, respectively, but with the concentrations increased by factors of 2, 4, and 8, the amount of aerosol increased essentially

linearly with increasing SO_2 concentrations at the higher concentration levels. The slope was less at the low concentration level.

In irradiations of mixtures of 2-pentene, NO_2, SO_2, and air with a residence time of 34 minutes, SO_2 disappeared rapidly, with equilibrium being reached in about 20 minutes. Aerosol formation was much slower; little light scattering was observed at 20 minutes, and maximum light scattering was measured at 90 minutes (Reckner and Scott, 1963).

The effect of concentration of NO on aerosol concentration is shown in Figure 2 (Harkins and Nicksic, 1965b). The main aerosol formation occurs shortly after conversion of NO to NO_2 is completed. Aerosol buildup continues until the ozone maximum is reached, then aerosol formation gradually decreases and levels off. The amount of aerosol formed at steady-state conditions appears to be approximately in line with the NO concentration, but at the ozone maximum there is an increase in aerosol as NO concentration increases from 0.5 ppm NO to 1 ppm followed by a decrease as it goes from 1 ppm to 2.0 ppm. The maximum aerosol at the ozone maximum occurred with 1 ppm NO.

Harkins and Nicksic (1965b) found that an increase in SO_2 concentration results in less hydrocarbon and less formaldehyde being formed in a given time. This effect must be slight, however, because in mixtures of 5 ppm propylene and 2 ppm NO the

rate of propylene oxidation decreased only by a factor of 2 to 3 when SO_2 was increased from 2 ppm to 1000 ppm. This was later confirmed by Altshuller, Kopczynski, et al. (1968). They irradiated mixtures of 2 ppm propylene, 0.5 ppm NO, and 0 to 1.12 ppm SO_2. As the SO_2 was increased, no significant differences were apparent in the rates of disappearance of propylene and NO or in the yields of oxidant, peroxyacetyl nitrate, formaldehyde, and acetaldehyde. The sulfate levels increased with increasing SO_2. The amount of SO_2 consumed decreased from 60% at lower initial SO_2 concentration to 25% at the higher levels but only 15 to 35 % of the SO_2 consumed could be accounted for as sulfate.

With the system 1-hexene(5ppm) - NO_2(1 ppm), Ripperton (1962) found a significant increase in the rate of SO_2 disappearance. Sixty to sixty-nine percent of the SO_2 was consumed in the hydrocarbon-NO_2-SO_2 system, as compared with 30% in the SO_2-O_2 system. His work also shows that the formation of oxidant is notably suppressed when SO_2 is added to the 1-hexene - NO_2 system.

Wilson and Levy (1968), however, found that with 1-butene (4 ppm) - NO(1 ppm) - SO_2(0 - 0.75 ppm) in relatively dry conditions the presence of SO_2 resulted in a general slowing down of photochemical smog reactions; the rate of conversion of NO to NO_2, the rate of disappearance of NO_2, the rate of production of ozone, and the maximum reaction rate of 1-butene all decreased.

The induction time for 1-butene increased. However, the maximum ozone concentration increased. Some of these effects are shown in Figures 3 through 7. (These figures are discussed in more detail later.) The maximum light-scattering signal, presumably aerosol, was very low except with an SO_2 concentration of 0.75 ppm. The aerosol was not observed until after the NO_2 peak had been reached and the NO concentration had fallen to a very low value. The rate of decay of SO_2 greatly increased in the presence of 1-butene and NO. A typical reaction profile for the system 1-butene - NO - SO_2 in relatively dry conditions is shown in Figure 8.

Although the role of SO_2 in the photooxidation of hydrocarbon-NO systems is difficult to assess quantitatively, the literature does provide some indications from which a rough qualitative "picture" might be formed.

Prager et al. (1960) found that when SO_2 was present at the start of photolysis of a 2-pentene - NO_2 system, the greatest amount of particulates were formed. The longer the reaction had proceeded before SO_2 was introduced, the less aerosol was formed. The addition of SO_2 10 minutes after the start of irradiation reduced light scattering to 10 %; addition at 20 minutes reduced light scattering to 1 %. In photolysis of 2-pentene and NO_2 (no SO_2), the NO_2 was reduced to 40 % after 10 minutes and to about 10 % after 20 minutes. The investigators concluded that the aerosol was produced by reaction of SO_2 and an intermediate in the olefin-NO_2 reaction.

Harkins and Nicksic (1965b) found that in the hydrocarbon-NO-SO_2 system the main aerosol formation occurred shortly after conversion of NO to NO_2 was complete. At this point the NO_2 concentration was at its maximum and the production of oxygen atoms was also at a maximum. Buildup of particulates continued until the ozone maximum was reached, after which aerosol production gradually decreased and levelled off. When NO_2 was used instead of NO in photolysis, they obtained more intense light scattering without a delay or induction period. Prager et al. (1960) also found that in olefin-NO-SO_2 photooxidations little or no aerosol was formed until the NO was converted to NO_2 and that once ozone was produced, particulates accumulated rapidly. Thus, NO can be eliminated as an active species.

There are some indications that ozone is somehow involved in the formation of particulates. The reaction of O_3 with SO_2 produces no aerosol (Dunham, 1960). The reaction is thought to be too slow to be of any significance. Although straight-chain mono-olefins and 1,3-butadiene formed few or no particulates when reacted with O_3 in the dark, 1,5-hexadiene, cyclopentene, and cyclohexene formed a larger number from the reaction with O_3 in the dark (Prager et al., 1960). The oxidation of SO_2 ocurred at a comparable rate when SO_2 was reacted with ozone and hydrocarbons[3]. in the dark (Harkins and Nicksic,

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3. Harkins and Nicksic (1965b) are not specific about the identity of the hydrocarbons they used in these experiments but we assume that they were olefins such as trans-2-butene or propylene since much of their work was done with these olefins.

1965b). The rate depended strongly on ozone concentrations. It therefore seems that some intermediate in the O_3-hydrocarbon reaction is effective in promoting the oxidation of SO_2 and in the formation of particulates in hydrocarbon-NO_x-SO_2 systems. Several authors have proposed that this intermediate might be an alkyl, alkoxyl, peroxyalkyl, or peroxyacyl radical and that such reactions as SO_2 addition or oxygen atom transfer

$$R\cdot \ (RO\cdot, RO_2\cdot) + SO_2 \rightarrow RSO_2 \ (ROSO_2, RO_2SO_2) \qquad (53)$$

$$RO\cdot \ (RO_2\cdot) + SO_2 \rightarrow R\cdot \ (RO\cdot) + SO_3 \qquad (54)$$

could account for the enhancement (Harkins and Nicksic, 1965b; Leighton, 1961).

Reactions of type 54 could account for an increase in formation of sulfuric acid aerosol, and reactions of type 53 could explain the formation of carbonaceous aerosols such as sulfenic or sulfonic acids. Most evidence indicates that the aerosols formed from irradiation of hydrocarbons (C >4 or 5) in the presence of NO_x and SO_2 do not contain carbon; the work of Prager et al. (1960) shows, however, that irradiations of hydrocarbons (olefins with C >6) in the presence of NO_2 produce aerosols that are probably carbonaceous.

As a result of these speculations several recent reports have described studies of alkyl radical additions to SO_2. Good and Thynne (1967) studied the reaction of SO_2 with methyl radicals generated from the photolysis of azomethane (λ >3400 A)

and with ethyl radicals generated by the photolysis of diethyl ketone. The addition reaction of methyl radicals forming methylsulphonyl radicals was rapid at room temperature. The rate of this reaction was comparable with the rate of the three-body reaction of methyl radicals with oxygen. Table 5 compares reactivities of methyl and ethyl radicals with SO_2 and O_2. The similarity in the rates of SO_2 and O_2 with CH_3 radicals however, will be less at atmospheric conditions, where concentration of oxygen is 10^5 to 10^6 times greater than the concentration of SO_2. Thus, at $CH_3 = 10^{-14}$ mole/cm^3, $SO_2 = 10^{-11}$ mole/cm^3, $O_2 = 10^{-5}$ mole/cm^3, and $M = 10^{-5}$ mole/cm^3 (the CH_3 radical-O_2 reaction is a three-body process), log $R_{CH_3SO_2} = -15.3$, and log $R_{CH_3O_2} = -7.8$. Gall, Slater, and Calvert (1969) have shown that the mechanism of photolysis of azomethane in SO_2 mixtures is much more complicated than Good and Thynne assumed and that their conclusions concerning the rate constants of methyl radical-SO_2 reactions must be re-evaluated. Timmons (1969) investigated the alkyl radical addition to SO_2 using both CH_3 and CF_3 radicals. Scavenging of the CF_3 radicals by SO_2 is the slower process.

In summary, the rate of disappearance of SO_2 and the formation of aerosol increase when SO_2 is photolyzed in the presence of olefinic hydrocarbons and NO_x. However, the effect of SO_2 on the rate parameters in the hydrocarbon-NO_x system has not been explained. Indications are that some intermediate in the ozone-hydrocarbon reaction is effective in promoting the

oxidation of SO_2 and the formation of aerosols. Whether excited SO_2 is necessary for this reaction to be effective is not known.

Photochemical Reactions of SO_2-CO System

At a recent meeting, Heicklen (1969) put forth an interesting mechanism for the role of carbon monoxide in photochemical smog. This mechanism involves the oxidation of CO by hydroxyl radicals and the subsequent formation of hydroperoxide radicals. The hydroperoxide radicals can then participate in the oxidation of nitric oxide. Subsequently, Westberg and Cohen (1970) analyzed the data of Schuck and Doyle (1959) and were able to reproduce the experimental curves by means of a computer. The computer calculations show that the rate of hydrocarbon disappearance is not significantly altered by the addition of 100 ppm of CO but that the yields of peroxyacetyl nitrate, ozone, and formaldehyde are greater. Bufalini, Gay, and Kopczynski (1970) have found that the addition of CO to n-butane irradiated in the presence of nitric oxide enhances the rate of oxidation of nitric oxide. The mechanism put forth by Heicklen (1969) is apparently correct, and CO does facilitate the oxidation of nitric oxide. Whether the computer analysis of Westberg and Cohen (1970) is valid can be established only by experimentation. If experimental results verify that oxidant formation is enhanced by the presence of carbon monoxide, then it is entirely possible that the oxidation of SO_2, when it is present, is also affected. However, the photolysis of SO_2 and CO mixtures in the absence of O_2 is

apparently quite low. Timmons (1969) found a quantum yield of 0.005 for CO_2 formation at 25°C with equal pressures of SO_2 and CO; he observed only a slight increase with increasing CO pressure. The quantum yield for CO_2 formation was very low for all reactant pressures employed, and it decreased slightly with increasing temperature over the range of 25° to 150°C.

Effect of H_2O Concentration

The early work of Gerhard and Johnston (1955) indicated that relative humidity had little effect on the photooxidation of SO_2 alone in air. They found that the rate of SO_2 disappearance was essentially constant for a series of runs with 10 ppm SO_2 and relative humidities of 32, 46, 71, and 91 %. However, Renzetti and Doyle (1960) found that the quantum yield for sulfur dioxide consumption with SO_2 concentrations of 0.61 to 0.22 ppm in air of 50 % relative humidity decreased from 0.3 to 0.036 when SO_2 was photooxidized in a dry system and P_{SO_2} = 12.7 mm, P_{O_2} = 10.6 mm. They also found that humidity had a striking effect on light scattering. With an SO_2 concentration of 0.47 ppm, light scattering increased by a factor of 8 to 12 when the relative humidity was increased from 0% to 50%. Unfortunately the rate of SO_2 consumption was not measured in this set of experiments.

Endow, Doyle, and Jones (1963) obtained spectral data from aerosols generated from the 2-methyl-2-butene - NO_2 - SO_2 system. These data indicated that the relative contributions

of inorganic and organic components to the aerosol generated at 10 to 20 % relative humidity were different from those of aerosols generated at 50 % relative humidity. At 10 to 20 % relative humidity sulfuric acid was present in the collected material but the absorption attributable to inorganic nitrogen and particularly to unidentified components was much stronger.

Goetz and Pueschel (1967) investigated the system 1-octene (80 ppm) - NO_2 (60 ppm) - SO_2 (0, 2, 15, and 60 ppm) at relative humidities of 15 to 55 %. Results, shown in Figure 9, indicate a notable increase in light scattering as SO_2 was increased from 2 to 60 ppm after an initial inhibiting effect at SO_2 = 2 ppm. The increase was most pronouced at lower humidities; at high humidities it was only moderate. The inhibiting effect of relatively low SO_2 concentrations (2 ppm) was greater at higher relative humidities. The data, plotted as a function of relative humidity in Figure 10, show that light scattering decreased as relative humidity increased, at all concentrations of SO_2 employed. The indicated behavior of hygroscopic particles exposed to increasing humidity is to adsorb moisture amounting to a few molecular layers at low relative humidities; to dissolve as humidity increases, becoming saturated droplets and at the same time undergoing an abrupt size increase; and thereafter, as humidity increases still further, to grow larger and more dilute (Orr et al., 1958). It is entirely possible that the aerosols produced by Goetz and Pueschel at high humidities grew to such a size that deposition on the walls of the photochemical chamber

was occurring. No measurements were made, however, for sulfate on the reactor walls. The presence of inert nuclei did not affect the strong influence of humidity.

Figures 11 through 14, along with Figures 3 through 7, show the results of Wilson and Levy (1968) for the photooxidation of 1-butane (4 ppm) - NO (1 ppm) - SO_2 (0.75 ppm) at different relative humidities. The results obtained under dry conditions have been discussed. From Figures 3 through 7, the inhibiting influence of SO_2 on the 1-butene - NO reaction was less pronounced in the presence of H_2O. The maximum ozone concentration decreased as the relative humidity increased but it decreased with increasing SO_2 concentration (0 to 0.75 ppm) at high relative humidity (65%). This was in contrast to results at lower humidities, where the maximum ozone concentration increased with increasing SO_2 concentrations.

Although SO_2 has an inhibiting effect on the 1-butene - NO reaction, Figures 11, 12, and 13 show that H_2O has a general accelerating effect. The reaction time parameters in Figure 12 show a large increase in rate as humidity was increased from 0 to 22 % and smaller increases between 22 and 65 %. It should be pointed out that there has been some controversy in the past few years on the effect of water vapor on the olefin-NO reaction. Scott (1965) and Dimitriades (1967) reported that the reaction is much slower in dryer mixtures; however, Stephens and Price (1969) found no decrease in reactivity under dry conditions, and Bufalini and Altshuller (1969) found no difference in hydrocarbon

consumption when the relative humidity was increased from 5 to 50 %.

The effect of humidity on aerosol formation in Figure 14 is interesting. As the relative humidity increased, the amount of light scattering decreased until no aerosol appeared at 65% relative humidity. This agrees with the work of Goetz and Pueschel (1967). However, as the relative humidity increased, the aerosol was observed earlier in the reaction. Since aerosol formation was first observed at the maximum NO_2 concentration, the earlier appearance of aerosol is attributed to the accelerating effect of H_2O on the time to reach the maximum concentration of NO_2. Wilson and Levy (1968) suggest that since the formation of peroxyacylnitrates shows this same dependence, the peroxyacyl radical may be important in aerosol formation. However, they have neglected the influence of water vapor on the coagulation and size of the condensation nuclei. A count of the condensation nuclei as well as the light scattering of the aerosol as the humidity was increased would have been more informative. There is strong evidence that water vapor concentration affects the coagulation rate and size of the aerosol (Hayakawa, 1964; Orr et al., 1958; DallaValle et al., 1954).

Identity of Aerosols

Little work has been done on determining the chemical identity of aerosols. Part of the problem arises from the necessity of working with extremely small amounts of materials and the limitations of the available analytical instruments.

The aerosol from the simple system SO_2 and O_2 has been identified as H_2SO_4. No tests have been reported on the chemical identity of aerosols obtained in the SO_2-NO_x system. More than likely, the aerosol is sulfate also. Nitrosyl hydrogen sulfate could possibly be formed as an aerosol, but this compound is so unstable in the presence of H_2O that if it were formed it would immediately be converted into H_2SO_4.

Prager, et al. (1960) did not find enough non-gaseous products from irradiations at low concentrations to permit identification but did obtain enough material for infrared analysis at higher concentrations (200 ppm hydrocarbon, 40 ppm NO_2, and 40 ppm SO_2). The CCl_4 solution of the particulates obtained from irradiation of 2-pentene - NO_2 - SO_2 system gave a spectrum with C-H and carbonyl bands at 3.4 and 5.8 μ respectively. Major peaks were also obtained at 6.9, 7.3, 7.8, and 8.8 μ. Except for the 5.8 μ peak, these peaks were the same as those obtained from a CCl_4 solution of a copolymer between 2-pentene and SO_2. The spectra from the cyclohexene-NO_2 system and the cyclohexene-NO_2-SO_2 system were similar except that the major peaks could be attributed to a nitrate ester. The smaller bands could be identified with a cyclohexene-SO_2 copolymer. Earlier work by Mader et al. (1952) supports the presence of carbonaceous aerosols. Microchemical tests on the ether-soluble aerosols confirmed the presence of various oxygenated organic functional groups, such as aldehydes, ketones, and organic acids, and infrared analysis backed up the chemical findings.

Infrared spectra, microchemical analysis, and spot tests on aerosols produced by irradiation of the lower olefins (3 ppm ethylene, propylene, or isobutylene) in the presence of 1 ppm NO_2 and 0.5 ppm SO_2 at 50% relative humidity indicated that the principal constituent of the aerosol was sulfuric acid with a smaller concentration of nitrite-type material (Endow et al., 1963). Weight-loss studies of the aerosols indicated that considerable portion of the original aerosol sample may be material that either is volatile or decomposes to give volatile products. The work of Harkins and Nicksic (1965a) confirms the fact that aerosols produced by irradiation of the lower olefins in the presence of NO_x and SO_2 are not of organic composition. To test for the formation of organic aerosols 3 ppm of tagged propylene (the carbon atom on each side of the double band was labelled) or ethylene was irradiated with 2 ppm NO and 5 ppm SO_2. In every case, with or without SO_2, the total tracer count of the aerosol was within experimental error the same. Thus, Harkins and Nicksic conclude that SO_2 does not provide condensation nuclei for the growth of organic aerosol.

When NH_3 is present in the gas-phase reactants, the aerosol formed from all the hydrocarbons investigated, except cyclohexene and α-pinene, has been identified as predominatly $(NH_4)_2SO_4$. Cyclohexene and α-pinene formed aerosols that contained carbonaceous material as well as $(NH_4)_2SO_4$ (Groblicki and Nebel, 1969).

Although this area of research in air pollution is beset with technical problems due to the extremely small amounts of

material formed, more information is needed. Past work indicates that the aerosol formed from mixtures of the lower hydrocarbons with NO_x and SO_2 is predominantly sulfuric acid, whereas the higher olefinic hydrocarbons appear to produce carbonaceous aerosol also, possibly organic acids, sulfinic or sulfonic acids, nitrate-esters, etc. The chemical identity of these carbonaceous aerosols is of vast importance since photochemically formed aerosols are in the respirable size range. Size distribution curves for aerosol formed from the irradiation of dilute auto exhaust indicate that most of the particles are less than 0.25 μ (Doyle and Renzetti, 1958).

Heterogeneous Reaction Systems

When gas-phase photochemical reactions are carried out in the presence of foreign particles, the reaction system is then heterogeneous. These foreign particles can function in the system in several different ways. They may act as nucleation centers, which can grow during the reaction to many times their original mass by the accumulation of certain reaction products, or they may serve as catalysts whereby an interaction between the reactants and the surface of the particle can cause an increase in the reaction rate and/or an aerosol can originate on the particle surface because of a catalytic surface interaction of the reactant.

The effect of nucleating particles on photochemical aerosol formation has been investigated by Goetz and Pueschel (1965, 1967).

Their results for the 1-octene - NO_2 system in the molar concentration range of 3×10^{-5} to 1.5×10^{-5} (50 to 100 times higher than in the atmosphere) can be summarized as follows.

The photochemical reaction produces products of relatively low volatility, which tend to agglomerate and by so doing convert from the gaseous state into the aerocolloidal state by a process of autonucleation.

When monodisperse polystyrene latex nuclei ($d = 0.35\ \mu$) are present in the system, the nuclei act as centers upon which the low-volatile products accumulate. Thus the size of the nuclei increases substantially during the reaction. These experiments showed that a 10-fold higher nuclei concentration will produce under the same conditions 10 times the mass of total accumulant and that the presence of nuclei will suppress the autonucleation process. Thus, fog formation by the condensation of water vapor on nuclei seems to occur by a different growth process since the growth of the nuclei for the same degree of supersaturation in fog formation is inversely proportional to their concentration.

In the absence of nucleating particles, the rate of autonucleation depends largely upon the reactant concentration. Thus, if the reactant concentration is sufficiently high and the nuclei level is low, the formation of autonucleates will compete with the process whereby the low-volatile products accumulate on the nuclei. The latter process will be favored by lower reactant concentrations or higher concentrations of nuclei.

Preliminary results from variation of NO_2 and nuclei levels indicated that there may be a preferential association of the NO_2 molecules with the nuclei which causes the surface to become catalytically active and accumulation thereon to accelerate.

There have been some indications that heterogeneous reactions of SO_2 with airborne particulates could be much more rapid than homogeneous gaseous reactions of SO_2 in air. Urone et al. (1968) found that SO_2 in the presence of powdered oxides of aluminum, calcium, chrominum, iron, lead, and vanadium reacted within minutes even without ultraviolet irradiation. One of the most significant papers in this area of research was that of Goetz and Pueschel (1967). They surveyed the effect of SO_2 on the formation of aerosols, giving attention to the formation of "preferred reaction centers" as determined by the sequence in which the reactants enter the experimental system. They used the same concentrations of hydrocarbon (1-octene at 80 ppm) and NO_2 (60 ppm) under identical irradiation conditions for different concentrations of stable reaction centers (nuclei of pure H_2O, tap H_2O, and polystyrene latex) and SO_2 (0.03 to 60 ppm) at different relative humidity levels (15 to 70%). When no stable nuclei were present, 2 ppm of SO_2 caused a marked reduction in light scattering below the level observed when SO_2 was not present. This inhibiting effect of relatively small SO_2 concentrations was greater at higher relative humidities. Increasing the SO_2 concentration further reversed this inhibition. At low

humidities with the SO_2 concentration increasing to the concentration of NO_2, the aerosol level increased up to 5 times that observed in the absence of SO_2; at high humidities the aerosol level never increased above about 1-1/2 times the value observed without SO_2. In the presence of nuclei, aerosol formation followed the same pattern, i.e., inhibition in the presence of 2 ppm SO_2 and subsequent increase as SO_2 was further increased, and strong influence of water vapor.

Striking results were obtained when the sequence in which the reactants met was altered. In the absence of nuclei the effect of altering of the sequence was negligible, but it became quite significant when nuclei were present. In the absence of SO_2, contact of the nuclei with NO_2 prior to contact with 1-octene always produced more light scattering than was produced when there was no prior contact. In the presence of SO_2, primary contact of the nuclei with SO_2 caused the least reduction in light scattering at low SO_2 concentrations but caused the largest growth of aerosol level at higher SO_2 concentrations. Thus, the presence of nuclei is a dominant factor in the formation and growth of aerosol.

Smith, Wagman, and Fish (1969) studied reactions of SO_2 (no light source) with submicron particles of Fe_3O_4, Al_2O_3, lead oxides, and platinum. These particles were generated by an exploding-wire technique and were allowed to interact with sulfur-35 labelled SO_2 at ppm concentrations. Sorption of SO_2 by

Fe_3O_4 reached 3% at an initial SO_2 concentration of 6.2 ppm and 1.8×10^5 particles per cm^3, and sorption on Al_2O_3 particles was about 50% with an initial SO_2 concentration of 1 ppm. The lead oxides caused complete removal of gaseous SO_2 within 5 minutes after mixing. Preferential chemisorption was observed at low SO_2 concentrations, followed at higher concentrations by multilayered physical adsorption.

Heterogeneous reaction systems undoubtedly resemble atmospheric conditions more closely than do homogeneous systems. However, the interpretation of results obtained with such systems is a difficult task. The work reported to date strongly indicates that the presence of stable nuclei can be a dominant factor in the reaction system. The presence of reactive nuclei or particles of the transition metals should be even more influential because of the known catalytic activity of these metals.

Reactions of SO_2 in Solution

Reactions of SO_2 in solution are of interest because water droplets are present in fogs and mists. These water droplets are formed by growth around minute particles or nuclei. Since these nuclei may be water-soluble particles such as metal salts, reactions of SO_2 with these droplets have been of concern in air pollution studies. Junge (1952) concludes that most of the individual nuclei in continental aerosol are mixed nuclei composed of several substances, some of which are soluble and some insoluble, and that gas absorption often alters the original composition. Droplets of metal salt solutions, such as $MnSO_4$, are

effective catalysts for converting absorbed SO_2 into H_2SO_4 (Johnstone and Coughanowr, 1958).

The solubility of SO_2 in H_2O is higher than that of most gases because it dissociates into ions. In the absence of any other material, SO_2 is present in H_2O almost entirely as the bisulfite ion. Terraglio and Manganelli (1967) found that the rate of solution of SO_2 (0.3 to 3 ppm) was a function of the SO_2 concentration but the overall solubility of SO_2 did not follow Henry's Law. Johnstone and Lappla (1934) have shown, however, that the solubility of SO_2 in dilute solutions of H_2SO_4 does follow Henry's Law.

The available studies of SO_2 in solution may be classified in two categories according to the design of the experiments. In one type of experiment one of the reactants is dissolved in a solution and the other reactant is either bubbled through the solution or added directly as a solution. In the other type of experiment a gas of know concentration is allowed to come in contact with liquid drops or liquid aerosols containing dissolved metal salts. Ammonia is sometimes used as a reactant in these experiments. The rate of absorption or reaction of the gas with the liquid drop and/or the formation of sulfate or hydrogen ion is usually measured.

When SO_2-air mixtures in the ppm range were bubbled through solutions of metal salts (Junge and Ryan, 1958) or aqueous solutions of metal sulfate salts were added directly to aqueous solutions of SO_2 containing a constant oxygen concentration (Bracewell

and Gall, 1967), sulfate formation occurred only in the salt solutions and negligible sulfate formation occurred in pure water. Sulfate formation was measured in the first study and conductance was measured in the second study. The amount of sulfate increased with time for a period of time, after which it leveled off to a final value. When a pH of about 2.2 was reached, the formation of sulfate stopped. The magnitude of the final value of sulfate was found to be a linear function of the SO_2 concentration; the highest final value of sulfate was obtained with solutions containing $MnCl_2$, followed by those containing $CuCl_2$ and $FeCl_2$.

The conductance curves were linear initally, then leveled off to a constant value. The initial reaction rate was linear with respect to SO_2 concentration and was 2 to 3 orders of magnitude greater for metal ions with five or six electrons in the 3d orbitals (Fe^{+2}, Fe^{+3}, and Mn^{+2}) than for other metal ions (Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, and Cr^{+3}). The suggestion is made that the reacting species is a metal-sulfito complex and that oxidation could occur through an oxygen addition compound, which rearranges to give an unstable sulfate complex.

Johnstone and Coughanowr (1958) found that the rate of formation of sulfuric acid in a drop of metal salt solution ($MnSO_4$, $Fe_2(SO_4)_3$, $CuSO_4$, and $NiSO_4$) suspended in air containing sulfur dioxide depends on the partial pressure of sulfur dioxide and on the nature and concentration of salt. Drops containing $MnSO_4$ were effective in promoting the absorption

and oxidation of SO_2. The investigators estimate that in a fog atmosphere containing 1 ppm SO_2 and 20-μ- diameter droplets formed on a 1-μ crystal and manganese sulfate, and with 4.8×10^7 droplets per cubic meter (equivalent to a water content of 0.2 gram per cubic meter), the rate of oxidation of SO_2 is 1% per minute. In their mathematical analysis they assumed a zero-order reaction with respect to SO_2. Moll (1959), however, observed a first-order reaction.

Matteson, Stöber, and Luther (1969) proposed the following mechanism for catalytic oxidation of SO_2 by aqueous aerosols of $MnSO_4$

$$SO_2 + Mn^{2+} \rightleftarrows Mn \cdot SO_2^{2+} \quad (55)$$

$$2Mn \cdot SO_2^{2+} + O_2 \rightleftarrows (Mn \cdot SO_2^{2+})2 \cdot O_2 \rightleftarrows 2Mn \cdot SO_3^{2+} \quad (56)$$

$$Mn \cdot SO_3^{2+} + H_2O \rightleftarrows Mn^{2+} + HSO_4^- + H^+ \quad (57)$$

$$HSO_4^- + H^+ \rightleftarrows H_2SO_4 \quad (58)$$

Rate constants for the rate of SO_2 disappearance (reaction 55) and for the initial rate of acid formation (reaction 57) were deduced to be

$$k_{55} = 2.3\text{-}2.5 \times 10^5 \ \ell \ \text{mole}^{-1} \ \text{min}^{-1}$$

$$k_{-55} = 9\text{-}11 \ \text{min}^{-1}$$

$$k_{57} = 0.21\text{-}0.23 \ \text{min}^{-1}$$

$$k_{-57} = 33\text{-}38 \ \ell^2 \ \text{mole}^{-2} \ \text{min}^{-1}$$

The primed rate constants include the constant H_2O concentration where appropriate and the ratio of the appropriate complex

steady-state concentration to the total steady-state concentration of all the complexes. A computer solution of the theoretical rate equations with the above rate constants adequately reproduced the experimental data. Although no humidity effect on the reaction could be established, the formation of acid below 95% relative humidity was practically nil. The authors calculate that in a stagnant air mass at 95% relative humidity and 10 ppm SO_2 and 1 μg $MnSO_4$ per cubic meter, 35 μg H_2SO_4 per cubic meter will be formed after 24 hours.

Georgii (1967) investigated the incorporation of sulfur dioxide into fog and rain droplets. A continuous rain of water was generated in a chamber containing 0.3 ppm SO_2. The intensity of the rain and the size of the droplets were varied. The decrease of SO_2 occurred more rapidly as the intensity of the rain was increased; at constant intensity, the half-lifetime of SO_2 in the chamber was longer as the size of the droplets was increased. The half-lifetime of SO_2 decreased from 25 minutes for droplets with mean-volume radii of 0.85 mm to 2.5 minutes for droplets with mean-volume radii of 0.01 mm. For a given intensity and droplet radius, the effectiveness of the rain in removing sulfur dioxide was dependent upon the pH value of the rain. The half-lifetime of SO_2 in the presence of cloud-droplets of 0.01 mm radii was much shorter than in the presence of raindrops.

Conclusion

Extrapolation of results obtained from laboratory experiments, even those specifically designed to simulate the atmosphere, to the actual environment cannot be done quantitatively. The atmosphere is essentially an "open" reaction system, in which not only do the gas-phase reactants and their interactions with oxygen and themselves define the presence of smog but also the complex meteorological conditions determine the extent and duration of smog. Fluctuating reactant concentrations, temperatures, humidities, and light intensities have not often been applied to the laboratory situations; this is understandable because results of laboratory experiments are often difficult enough to interpret without the additional problem of constantly changing conditions. The effects of sulfur dioxide on health, visibility, materials, and vegetation have been discussed in the "Air Quality Criteria for Sulfur Oxides" document of the U. S. Department of Health, Education, and Welfare (1969). Laboratory studies of these effects, in particular, are subject to the above criticism. Even so, analysis of available data clearly indicates an association between air pollution, as measured by sulfur dioxide, and adverse effects on health, visibility, plants, and materials.

With the advent of programs designed to control pollutant emissions, changes in the nature and not just the level of smog will occur. Stephens and Price (1969) point out that when hydrocarbon emissions are controlled to such an extent that

the amount of reactive hydrocarbon is no longer sufficient to convert all the nitric oxide to products then, although a marked decrease in most smog symptoms should be observed, an appreciable increase in nitrogen dioxide may occur.

At present the degree to which sulfur dioxide interacts with reactive hydrocarbons and nitrogen oxides, and the mechanisms by which aerosols are formed, are not well understood. Experimental results on aerosol formation involving other pollutants, such as H_2S, NH_3, and NO_2, are even more meager than those involving SO_2. There have been relatively few in-depth studies of mechanisms of aerosol formation from air pollutants. The magnitude of the problem is indicated by the fact that the gas-phase photochemical reactions of nitrogen oxides and hydrocarbons have been studied by many investigators since the early 1950's and as of yet there is no clear quantitative understanding of the mechanisms although there have been many significant contributions. As government continues to focus upon environmental problems and public awareness and demand for cleaner air increase, it is hoped that more research will be directed toward the interactions of sulfur dioxide and other pollutants in the atmosphere. Control of any pollutant in a complex system like the atmosphere involves not only an understanding of the intricate reactions but also an awareness of the consequences of all control measures. This aspect of the problem should be considered fully in future air pollution research programs.

REFERENCES

Air Pollution Control District, County of Los Angeles, "Effectiveness of Organic Solvents in Photochemical Smog Formation". Solvent Project, Final Report, 1966.

Altshuller, A.P. and Bufalini, J.J., Photochem. Photobiol. 4, 97 (1965).

Altshuller, A.P. and Bufalini, J.J., submitted for publication in Environ. Sci. Technol. (1970).

Altshuller, A.P. and Cohen, R.R., Presented at American Chemical Society Meeting, Division of Water, Air and Waste Chemistry, New York, New York, Sept. 8-13, 1963.

Altshuller, A.P., Klosterman, D.L., Leach, P.W., Hindawi, I.J., and Sigsby, J.E., Jr., Intern. J. Air Water Pollution 10, 81 (1966).

Altshuller, A.P., Kopczynski, S.L., Lonneman, W.A., Becker, T.L., and Wilson, D.L., Environ. Sci. Technol. 2, 696 (1968).

Billings, C.E., Berger, A.W., Dennis, R., Driscoll, J., Lull, D., and Warneck, P., "Study of Reactions of Sulfur in Stack Plumes," Contract No. PH-86-67-125, GCA Corporation, Bedford, Massachusetts, First Annual Report, 1968.

Blacet, F.E., (1950) reference in Gerhard, E.R. and Johnstone, H.F., Ind. Eng. Chem. 47, 972 (1955).

Blacet, F.E., Ind. Eng. Chem. 44, 1339 (1952).

Blacet, F.E., (1959) reference in Renzetti, N.A. and Doyle, G.J., Intern. J. Air Pollution 2, 327 (1960).

Bracewell, J.M. and Gall, D., "Proceedings of the Symposium on the Physico-chemical Transformation of Sulfur Compounds in the Atmosphere and the Formation of Acid Smogs," Meteorologish-Geophysikalishes Institut, Johannes Gutenberg Universitat, Mainz, Germany, June 8-9, 1967.

Bufalini, J.J. and Altshuller, A.P., Environ. Sci. Technol. 3, 469 (1969).

Bufalini, J.J., Gay, B. and Kopczynski, S.L., submitted for publication in Environ. Sci. Technol. (1970).

Bufalini, J.J. and Stephens, E.R., Intern. J. Air Water Pollution 9, 123 (1965)

Clyne, M.A.A., Halstead, C.J. and Thrush, B.A., Proc. Roy. Soc. (London), Series A, 295, 355 (1966).

Dainton, F.S. and Ivin, K.J., Trans. Faraday Soc., 46, 374, 382 (1950).

DallaValle, J.M., Orr, C., Jr., and Hinkle, B.L., British J. of Appl. Physics, H-203 (1954).

Dimitriades, F., J. Air Pollution Control Assoc. 17, 460 (1967).

Doyle, G.J. and Renzetti, N.A., J. Air Pollution Control Assoc. 8, 23 (1958).

Dunham, S.B., Nature 188, 51 (1960).

Endow, N., Doyle, G.J. and Jones, J.L., J. Air Pollution Control Assoc. 13, 141 (1963).

Fajans, E. and Goodeve, C.F., Trans. Faraday Soc. 32, 511, (1936).

Ford H.W., Doyle, G.J. and Endow, N., J. Chem. Phys. 26, 1336 (1957).

Gall, J.W., Slater, D.H. and Calvert, J.G., Presented at General Motors Research Laboratories Symposium on Chemical Reactions in Urban Atmospheres, General Motors Corporation, Warren, Michigan, Oct. 6-7, 1969.

Gerhard, E.R. and Johnstone, H.F., Ind. Eng. Chem.47, 972 (1955).

Georgii, Hans-Walter, "Proceedings of the Symposium on the Physico-chemical Transformation of Sulfur Compounds in the Atmosphere and the Formation of Acid Smogs," Meteorologish-Geophysikalisches Institut, Johannes Gutenberg Universitat, Mainz, Germany, June 8-9, 1967.

Goetz, Alexander and Pueschel, R.F., J. Air Pollution Control Assoc. 15, 90 (1965).

Goetz, A. and Pueschel, R., Atmos. Environ. 1, 287 (1967).

Good, A. and Thynne, J.C.J., Trans Faraday Soc. 63, 2708, 2720 (1967).

Greig, J.D. and Hall, P.G., Trans. Faraday Soc. 62, 652 (1966).

Groblicki, P.J. and Nebel, G.J., Presented at General Motors Research Laboratories Symposium on Chemical Reactions in Urban Atmospheres, General Motors Corporation, Warren, Michigan, Oct. 6-7, 1969.

Hall, T.C., Jr., Ph.D. Thesis, University of California, Los Angeles, California, 1953.

Halstead, C.J. and Thrush, B.A., Nature 204, 992 (1964).

Halstead, C.J. and Thrush, B.A., Proc. Roy. Soc. (London), Series A, 295, 363 (1966).

Harkins, J. and Nicksic, S.W., a. J. Air Pollution Control Assoc. 15, 218 (1965). b. Presented before the Division of Petroleum Chemistry, American Chemical Society, Detroit, Michigan, April 4-9, 1965.

Hayakawa, Ichiya, J. Air Pollution Control Assoc. 14, 339 (1964).

Heicklen, J., Presented at General Motors Research Laboratories Symposium on Chemical Reactions in Urban Atmospheres, General Motors Corporation, Warren, Michigan, Oct. 6-7, 1969.

Hoare, D. E. and Walsh, A.D., Trans. Faraday Soc. 53, 1102 (1957).

Jacobs, M.B., "The Chemical Analysis of Air Pollutants," p. 180, Interscience Publishers, New York, New York, 1960.

Jaffee, S. and Klein, F.S., Trans. Faraday Soc. 62, 2150 (1966).

Johnston, H.S. and der Jain, K., Science 131, 1523 (1960).

Johnston, H.S. and Yost, P.M., J. Chem Phys. 17, 366 (1949).

Johnstone, H.F. and Coughanowr, D.R., Ind. Eng. Chem. 50, 1169 (1958).

Johnstone, H.F. and Lappla, P.W., J. Amer. Chem. Soc. 56, 2233 (1934).

Jolley, J.E., J. Amer. Chem. Soc. 79, 1537 (1957).

Junge, C.E., Ann. Meteorol., Beiheit, (1952).

Junge, C. E. and Ryan, T.G., Quart. J. Roy. Meteorol. Soc. 84, 46 (1958).

Kaufman, F., Progress in Reaction Kinetics 1, 3 (1961).

Kopczynski, S. L. and Altshuller, A.P., Intern. J. Air Water Pollution 6, 133 (1962).

Leighton, P.A., "Photochemistry of Air Pollution," Academic Press, New York, New York, 1961.

Mader, P.P., MacPhee, R.D., Lofberg, R.T. and Larson, G.P., Ind. Eng. Chem. 44, 1352 (1952).

Matteson, Michael J., Stöber, Werner, and Luther, Horst, Ind. Eng. Chem. Fundametals 8, 677 (1969).

Moll, A.J., "Formation of Sulfuric Acid in Artificial Fogs," B.S. Thesis, University of Illinois, 1959.

Mulcahy, M.F.R., Stevens, J.R. and Ward, J.C., J. Phys. Chem. 71, 2124 (1967).

Noyes, W.A. and Leighton, P.A., "The Photochemistry of Gases," p. 400, Reinhold Publishing Corp., New York, New York, 1941.

Ogata, Y., Izawa, Y. and Tsuda, T., Tetrahedron 21, 1349 (1965).

Okuda, S., Rao, T.N., Slater, D.H. and Calvert, J.G., J. Phys. Chem. 73, 4412 (1969).

Orr, Clyde, Jr., Hurd, F. Kenneth and Corbett, William J., J. Colloid Sci. 13, 472 (1958).

Pitts, J.N., Jr., Sharp, J.H., Chang, S.I., J. Chem. Phys. 39, 238 (1963).

Prager, Manfred J., Stephens, Edgar R. and Scott, William E., Ind. Eng. Chem. 52, 521 (1960).

Rao, T. Navaneeth, Collier, Susan S. and Calvert, Jack G.,
a. J. Amer. Chem. Soc. 91, 1609 (1969).
b. J. Amer. Chem. Soc. 91, 1616 (1969).

Reckner, Louis and Scott, W.E., Presented at American Chemical Society Meeting, Division of Water, Air, and Waste Chemistry, New York, New York, Sept. 8-13, 1963.

Renzetti, N.A. and Doyle, G. J., Intern. J. Air Pollution 2, 327 (1960).

Ripperton. L.A., Decker, C.E. and Page, W.W., Presented at American Chemical Society Meeting, Division of Water, Air, and Waste Chemistry, Atlantic City, New Jersey, Sept. 13-17, 1962.

Rolfes, T.R., Reeves, R.R., Jr. and Harteck, P., J. Phys. Chem. 69, 849 (1965).

Sato, S. and Cvetanovic, R.J., Can. J. Chem. 36, 279, 970, 1668 (1958).

Schuck, E.A. and Doyle, G.J., "Photooxidation of Hydrocarbons in Mixtures Containing Oxides of Nitrogren and Sulfur Dioxide," Report No. 29, Air Pollution Foundation, San Marino, California 1959.

Schuck, E.A., Stephens, E.R. and Schrock, R.R., Presented at the 59th Annual Meeting of APCA, San Francisco, Calif., June 20-24, 1966.

Scott, W.E., (1965) reference in Stephens, Edgar R. and Price, Monty A., Atmos. Environ. 3, 573 (1969).

Sethi, D.S., Allen, E.R. and Cadle, R.D., Abstracts of Fifth International Conference on Photochemistry, IBM Watson Research Center, Yorktown, New York, Sept. 2-5, 1969.

Sharma, A., Padur, J.P. and Warneck, P., J. Phys. Chem. 71, 1602 (1967).

Smith, B.M., Wagman, J. and Fish, B.R., Environ. Sci. Technol. 3, 558 (1969).

Stephens, Edgar R. and Price, Monty A., Atmos. Environ. 3, 573 (1969).

Stern, A.C., Editor, "Air Pollution," Vol. I, II and III, 2nd Edition, Academic Press, New York, New York, 1968.

Stevenson, H.J.R., Sanderson, D.E. and Altshuller, A.P., Intern. J. Air Water Pollution 9, 367 (1965).

Strickler, S.J. and Howell, D.B., J. Chem. Phys. 49, 1947 (1968).

Terraglio, F.P. and Manganelli, R.M., J. Air Pollution Control Assoc. 17, 403 (1967).

Timmons, R.G., Presented at General Motors Research Laboratories Symposium on Chemical Reactions in Urban Atmospheres, General Motors Corporation, Warren, Michigan, Oct. 6-7, 1969.

Trotman-Dickenson, A.F., "Gas Kinetics," p. 249, Academic Press, Inc., New York, New York, 1955.

Urone, Paul, Lutsep, Helmut, Noyes, Claudia M. and Parcher, Jon F., Environ. Sci. Technol. 2, 611 (1968).

Urone, Paul and Schroeder, William H., Environ. Sci. Technol. 3, 436 (1969).

U. S. Department of Health, Education, and Welfare, "Air Quality Criteria for Sulfur Oxides," National Air Pollution Control Administration Publication No. AP-50, Washington, D. C., 1969.

Walsh, A.D., J. Chem. Soc., 2266 (1953).

Wilson, William E., Jr. and Levy, Arthur, "A Study of Sulfur Dioxide in Photochemical Smog," Annual Progress Report to American Petroleum Institute, Project S-11, Battelle Memorial Institute, Columbus, Ohio, 1968.

Westberg, K. and Cohen, N., Submitted for publication to Intern. J. Chem. Kinetics (1970).

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Table 1. Primary Reactions of Sulfur Dioxide[a]

Reaction[b]	Rate Constant[c]	Reaction Number
$SO_2 + h\nu \rightarrow {}^1SO_2$	$\Phi I_{absorbed}$	(1)
${}^1SO_2 + SO_2 \rightarrow (2SO_2)$	$2.0 \pm 1.0 \times 10^{10}$ ℓ mole^{-1} sec^{-1}	(2)
${}^1SO_2 + SO_2 \rightarrow {}^3SO_2 + SO_2$	$0.18 \pm 0.08 \times 10^{10}$ ℓ mole^{-1} sec^{-1}	(3)
${}^1SO_2 \rightarrow SO_2 + h\nu_f$	$5.1 \pm 4.0 \times 10^{3}$ sec^{-1}	(4)
${}^1SO_2 \rightarrow SO_2$	$1.7 \pm 0.4 \times 10^{4}$ sec^{-1}	(5)
${}^1SO_2 \rightarrow {}^3SO_2$	$1.5 \pm 0.8 \times 10^{3}$ sec^{-1}	(6)
${}^3SO_2 \rightarrow SO_2 + h\nu_p$	$0.10 \pm 0.06 \times 10^{2}$ sec^{-1}	(7)
${}^3SO_2 \rightarrow SO_2$	$1.3 \pm 0.2 \times 10^{2}$ sec^{-1}	(8)
${}^3SO_2 + SO_2 \rightarrow (2SO_2)$	$2.5 \pm 0.5 \times 10^{7}$ ℓ mole^{-1} sec^{-1}	(9)

[a] Rao, Collier, and Calvert, 1969a.

[b] Parentheses were used in reactions 2 and 9 to designate that either chemical change or relaxation to ground state molecules was occurring.

[c] The rate constant for reaction 9 was calculated by Rao, Collier and Calvert (1969a) from the data of Strickler and Howell (1968).

Table 2. Effect of Irradiation on Aerosol Formation in Nitrogen Dioxide-Hydrocarbon Reactions[a]

(Reactant concn., ppm: olefin, 10; NO_2, 5; SO_2, 2)

Hydrocarbon	Photometer Reading Incr.[b] Olefin-NO_2	Olefin-NO_2-SO_2
Ethylene	0.1	2.2
1-Butene	0.05	2.85
2-Butene	0.05	3.0
2-Methylpropene	0.0	
1-Pentene	0.1	3.05
2-Pentene	0.0	3.0
3-Methyl-1-butene	0.1	
1-Hexene	0.05	3.35
2-Hexene	0.25	3.05
cis-3-Methyl-2-pentene	0.2	
3-Heptene	0.45	3.35
2,4,4-Trimethyl-1-pentene	3.3	3.3
n-Butane		0.1
2-Methylpentane		0.0

[a] [b] Prager et al., 1960.
Average of three determinations for straight-chain olefins. Reading before irradiation subtracted from readings during irradiation.

Table 3. Aerosol Formation by Systems Containing Diolefins[a]

(Reactant concn., ppm: nydrocarbon, 10; NO_2, 5; SO_2, 2; O_3, 5)

System	Photometer Readings		
	Trial 1	Trial 2	Trial 3
1,3-Butadiene, NO_2[b]	1.0	1.3	
1,3-Butadiene, NO_2, SO_2[b]	3.2		
1,3-Butadiene, O_3[c]	0.25	0.0	0.0
1,5-Hexadiene, NO_2[b]	3.7	3.6	
1,5-Hexadiene, NO_2, SO_2[b]	3.9	3.95	
1,5-Hexadiene, O_3[c]	3.2	3.2	

[a]Prager et al., 1960

[b]Irradiated

[c]Dark

Table 4. Aerosol Formation by Systems Containing Cyclic Hydrocarbons[a]

(Reactant concn., ppm: hydrocarbon, 10; NO_2, 5; SO_2, 2; O_3, 5)

System	Photometer Readings		
	Trial 1	Trial 2	Trial 3
Cyclopropane, NO_2[b]	0.3	0.0	
Cyclopentene, NO_2[b]	2.75	2.5	
Cyclohexane, NO_2[b]	0.0		
Cyclohexene NO_2[b]	3.65	3.7	3.2
Cyclohexene, NO_2, SO_2[b]	3.5		
Cyclohexene, NO, SO_2[b]	3.75		
Dicyclopentadiene, NO_2[b]	4.35	4.35	
Dicyclopentadiene, NO_2, SO_2[b]	3.9		
Cyclopentene, O_3[c]	2.7		
Cyclohexene, O_3[c]	3.35		

[a] Prager et al., 1960
[b] Irradiated
[c] Dark

Table 5. Comparison of Arrhenius Parameters, Velocity Constants, and Rates of Formation of RX at 25°C for the Reaction: $R + X(+M) \rightarrow RX(+M)$[a]

R	X	log A $mole^{-1}\ cm^3\ sec^{-1}$	E kcal $mole^{-1}$	log k(25°C) $mole^{-1}\ cm^3\ sec^{-1}$	log R_{RX}	Reference
CH_3	SO_2	10·82	1·5	9·7	− 11·3	Good & Thynne, 1967
C_2H_5	SO_2	11·0	3·1	8·6	− 12·4	Good & Thynne, 1967
CH_3	O_2	16·18[b]	0	16·18[b]	− 10·8	Hoare & Walsh, 1957
C_2H_5	O_2	10·7	0	10·7	− 10·4	Jolley, 1957

[a]Good and Thynne, 1967.

[b]Units of k and A: $mole^{-2}\ cm^6\ sec^{-1}$, calculated using $[R] = 10^{-14}$, $[M] = 10^{-6}$, $[X] = 10^{-7}$, mole cm^{-3}; R_{RX} in mole $cm^{-3}\ sec^{-1}$.

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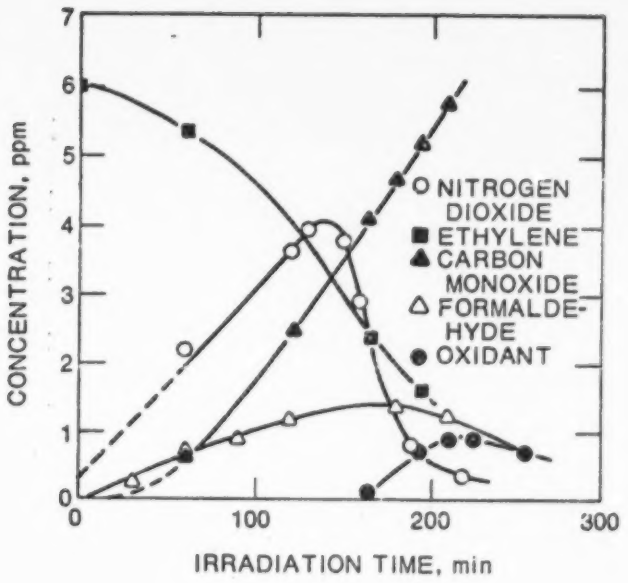
CONCENTRATION, ppm
IRRADIATION TIME, min
0
1
2
3
4
5
6
7
0
100
200
300
NITROGEN DIOXIDE
ETHYLENE
CARBON MONOXIDE
FORMALDE-HYDE
OXIDANT

FIGURE 1

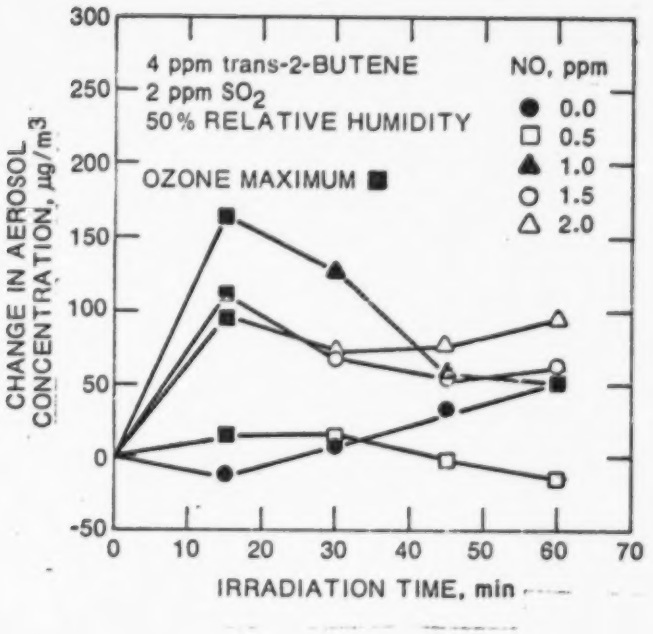
4 ppm trans-2-BUTENE
2 ppm SO_2
50% RELATIVE HUMIDITY
OZONE MAXIMUM ■
NO, ppm
● 0.0
□ 0.5
▲ 1.0
○ 1.5
△ 2.0
CHANGE IN AEROSOL CONCENTRATION, μg/m³
300
250
200
150
100
50
0
-50
0
10
20
30
40
50
60
70
IRRADIATION TIME, min

FIGURE 2

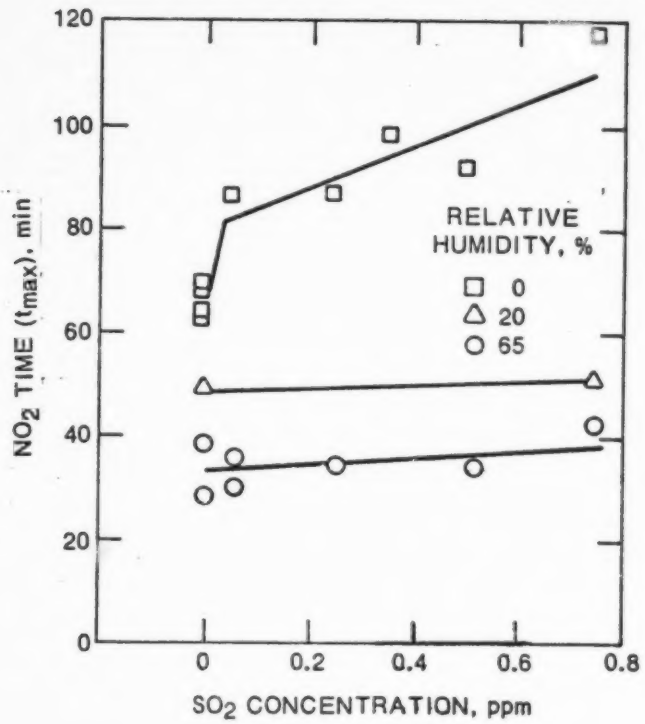
120
100
80
60
40
20
0
NO_2 TIME (t_{max}), min
RELATIVE HUMIDITY, %
0
20
65
0
0.2
0.4
0.6
0.8
SO_2 CONCENTRATION, ppm

FIGURE 3

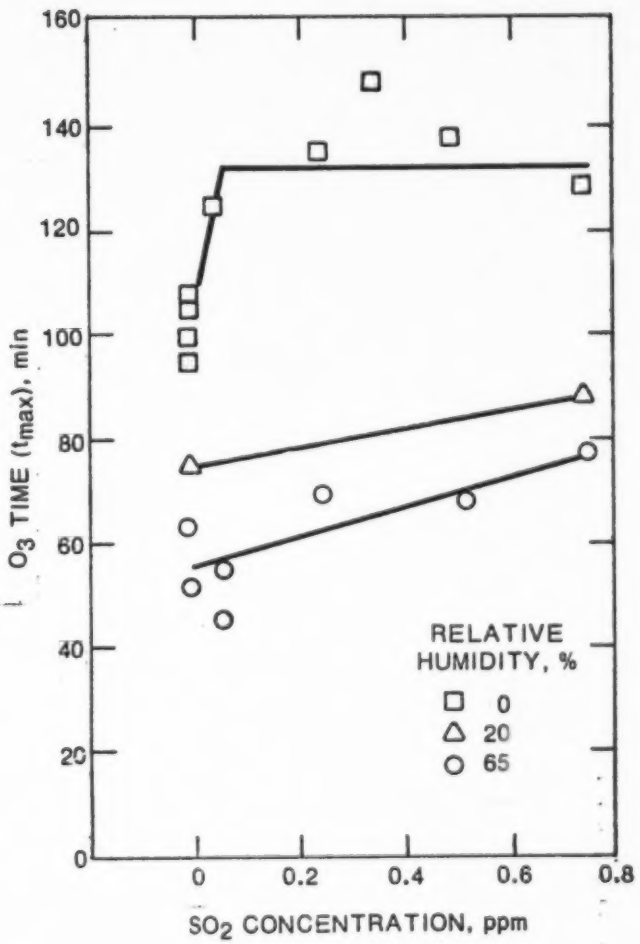
160
140
120
100
80
60
40
20
0
O_3 TIME (t_{max}), min
0
0.2
0.4
0.6
0.8
SO_2 CONCENTRATION, ppm
RELATIVE HUMIDITY, %
0
20
65

FIGURE 4

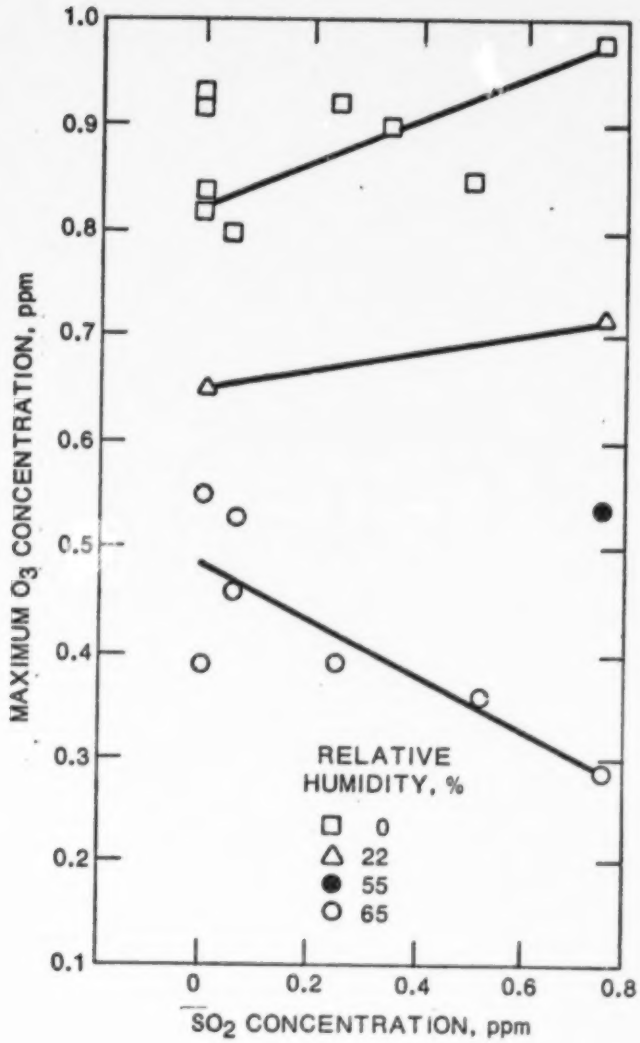
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
MAXIMUM O_3 CONCENTRATION, ppm
0
0.2
0.4
0.6
0.8
SO_2 CONCENTRATION, ppm
RELATIVE HUMIDITY, %
0
22
55
65

FIGURE 5

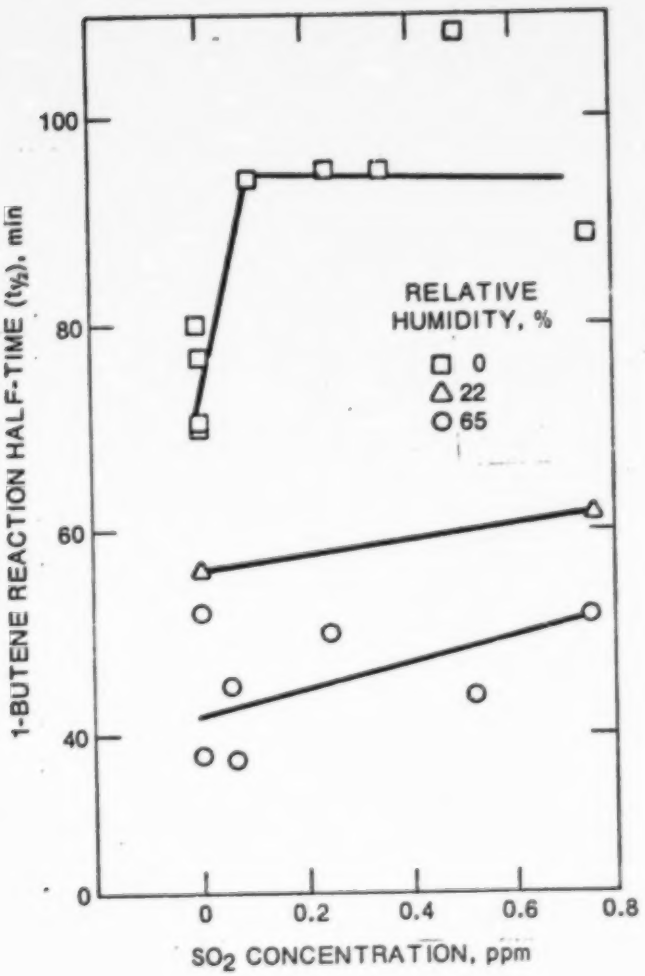
1-BUTENE REACTION HALF-TIME ($t_{½}$), min
100
80
60
40
0
0
0.2
0.4
0.6
0.8
SO_2 CONCENTRATION, ppm
RELATIVE HUMIDITY, %
0
22
65

FIGURE 6

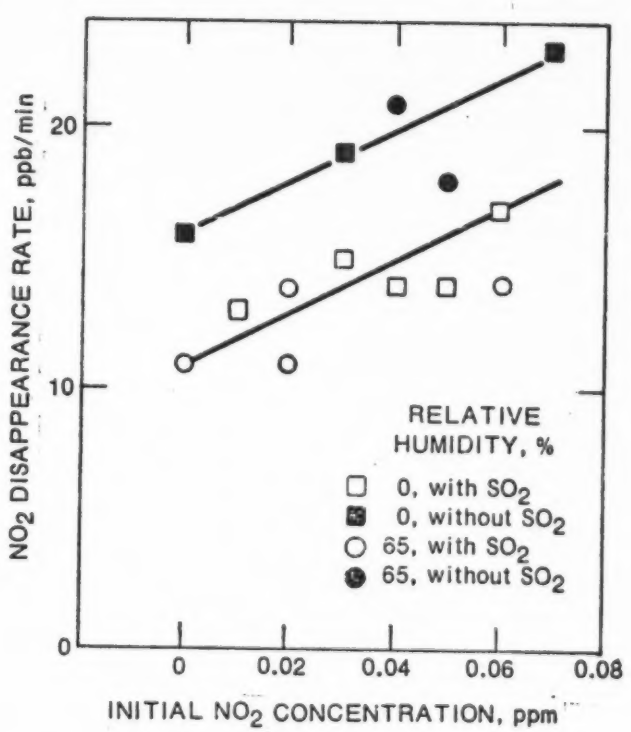
NO_2 DISAPPEARANCE RATE, ppb/min
20
10
0
0
0.02
0.04
0.06
0.08
INITIAL NO_2 CONCENTRATION, ppm
RELATIVE HUMIDITY, %
0, with SO_2
0, without SO_2
65, with SO_2
65, without SO_2

FIGURE 7

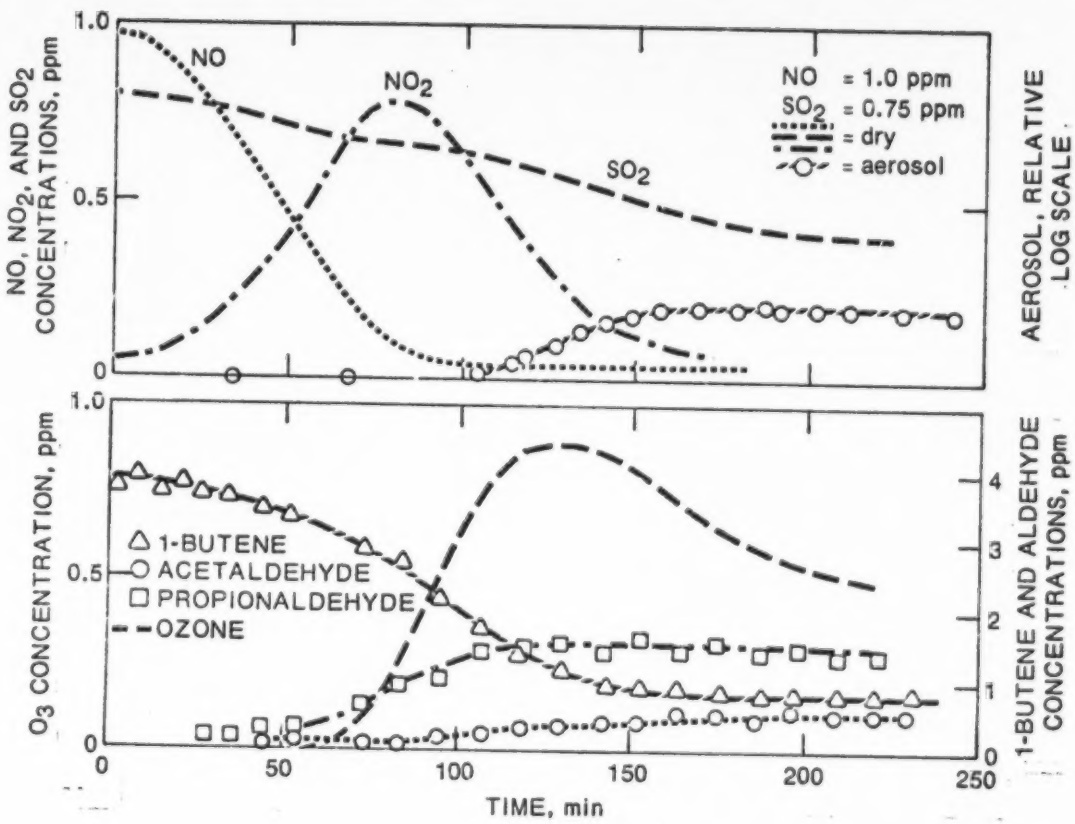
NO, NO2, AND SO2 CONCENTRATIONS, ppm
AEROSOL, RELATIVE LOG SCALE
NO
NO2
SO2
NO = 1.0 ppm
SO2 = 0.75 ppm
= dry
= aerosol
O3 CONCENTRATION, ppm
1-BUTENE AND ALDEHYDE CONCENTRATIONS, ppm
1-BUTENE
ACETALDEHYDE
PROPIONALDEHYDE
OZONE
TIME, min

FIGURE 8

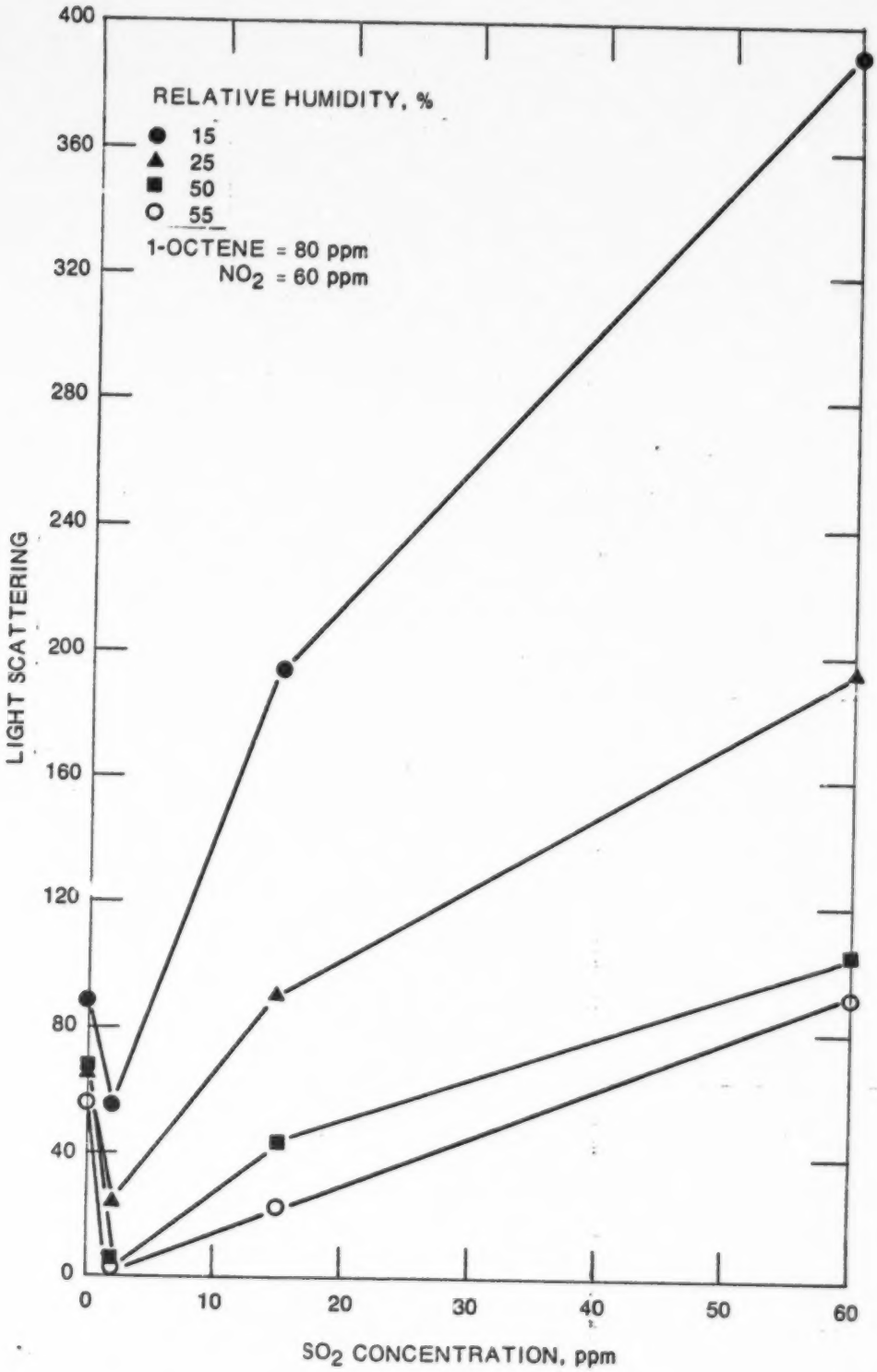
RELATIVE HUMIDITY, %
15
25
50
55
1-OCTENE = 80 ppm
NO_2 = 60 ppm
LIGHT SCATTERING
400
360
320
280
240
200
160
120
80
40
0
0
10
20
30
40
50
60
SO_2 CONCENTRATION, ppm

FIGURE 9

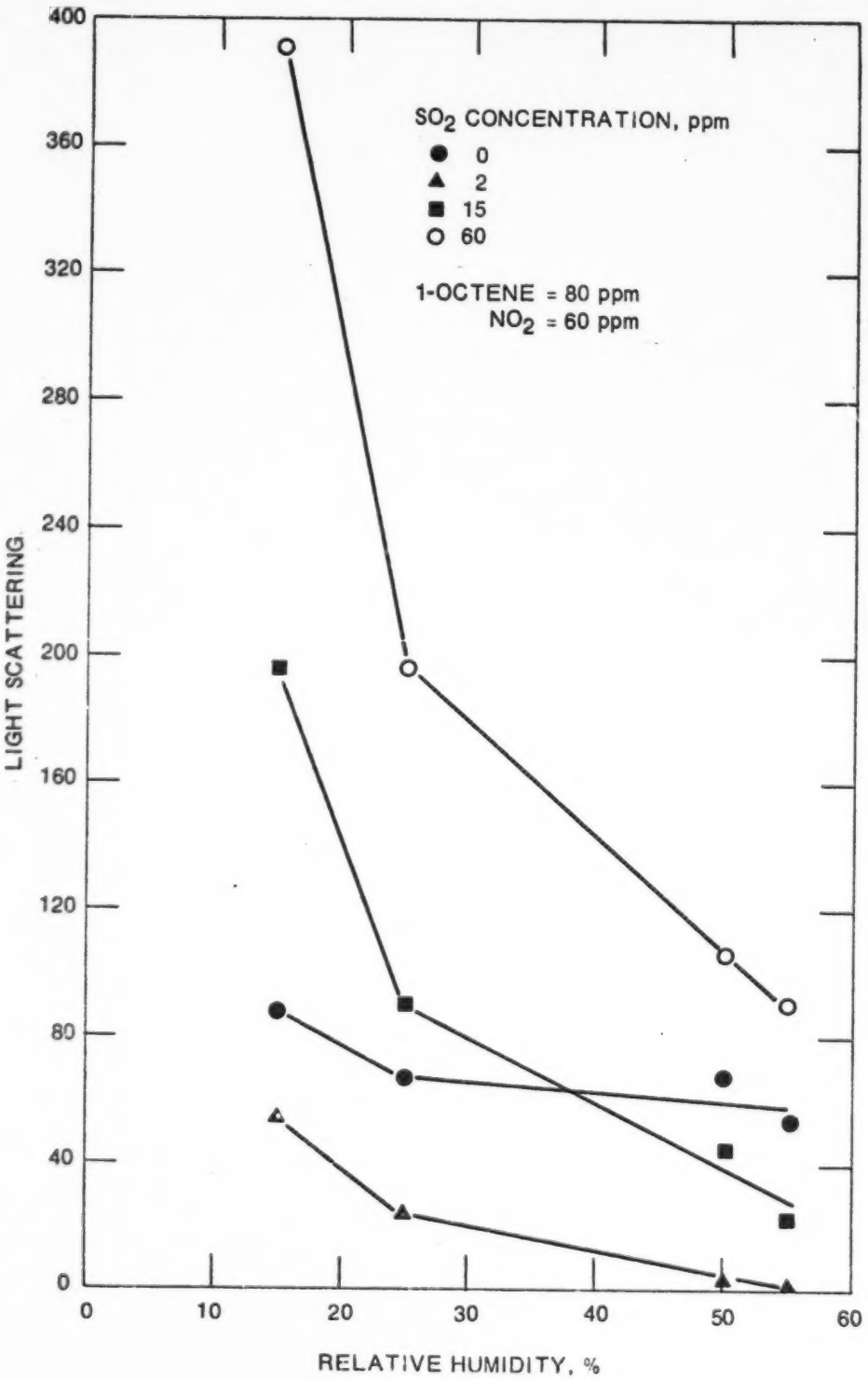
400
360
320
280
240
200
160
120
80
40
0
LIGHT SCATTERING
SO2 CONCENTRATION, ppm
0
2
15
60
1-OCTENE = 80 ppm
NO2 = 60 ppm
0
10
20
30
40
50
60
RELATIVE HUMIDITY, %

FIGURE 10

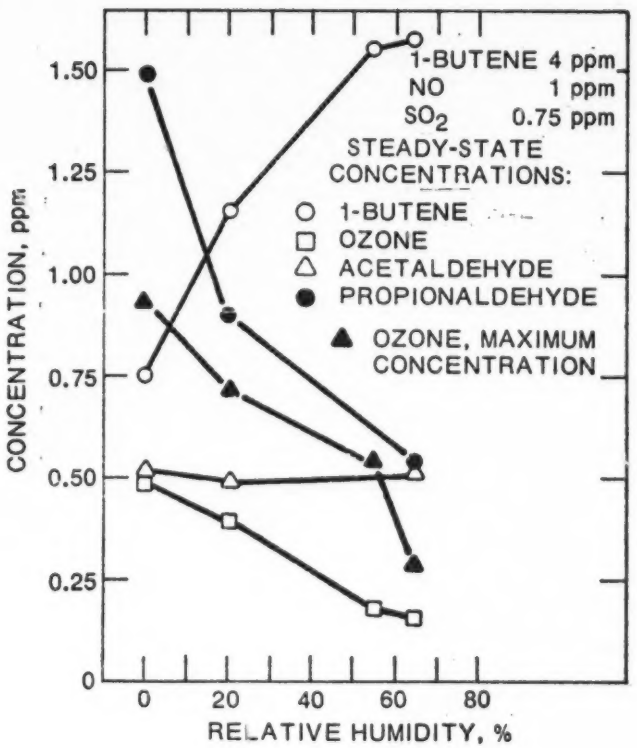
1-BUTENE 4 ppm
NO 1 ppm
SO_2 0.75 ppm
STEADY-STATE CONCENTRATIONS:
1-BUTENE
OZONE
ACETALDEHYDE
PROPIONALDEHYDE
OZONE, MAXIMUM CONCENTRATION
CONCENTRATION, ppm
1.50
1.25
1.00
0.75
0.50
0.25
0
0
20
40
60
80
RELATIVE HUMIDITY, %

FIGURE 11

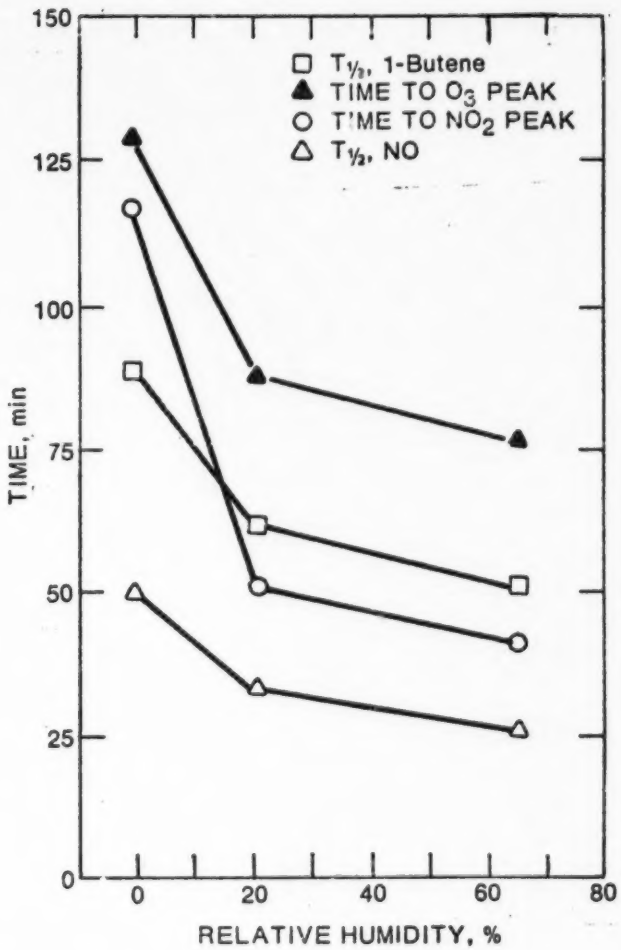
150
125
100
75
50
25
0
TIME, min
0
20
40
60
80
RELATIVE HUMIDITY, %
T½, 1-Butene
TIME TO O3 PEAK
T'ME TO NO2 PEAK
T½, NO

FIGURE 12

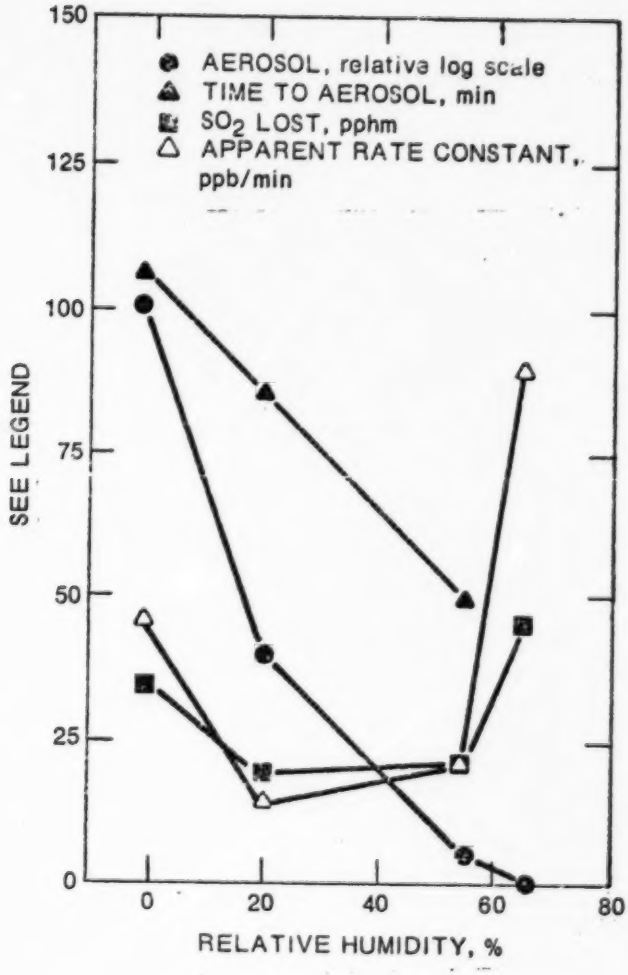
AEROSOL, relative log scale
TIME TO AEROSOL, min
SO_2 LOST, pphm
APPARENT RATE CONSTANT, ppb/min
SEE LEGEND
150
125
100
75
50
25
0
0
20
40
60
80
RELATIVE HUMIDITY, %

FIGURE 13

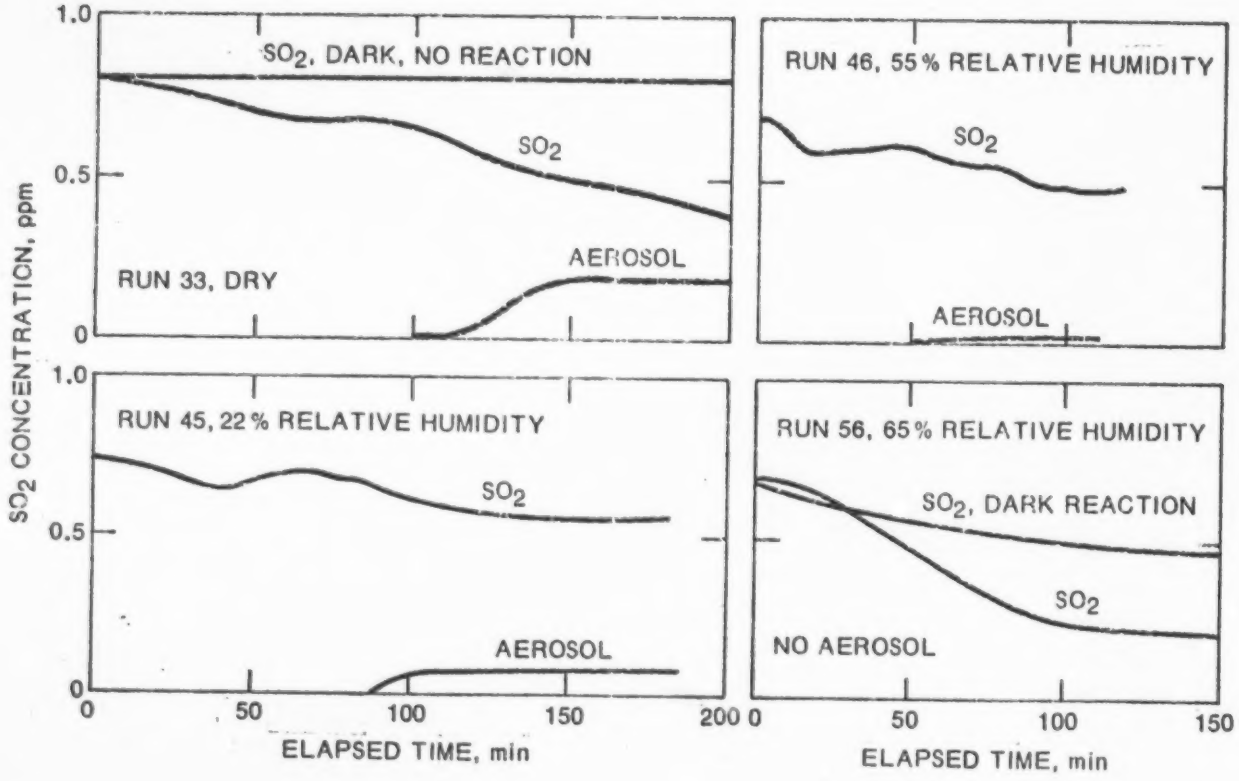
1.0
0.5
0
SO_2 CONCENTRATION, ppm
SO_2, DARK, NO REACTION
SO_2
AEROSOL
RUN 33, DRY
RUN 46, 55% RELATIVE HUMIDITY
SO_2
AEROSOL
RUN 45, 22% RELATIVE HUMIDITY
SO_2
AEROSOL
RUN 56, 65% RELATIVE HUMIDITY
SO_2, DARK REACTION
SO_2
NO AEROSOL
0
50
100
150
200
ELAPSED TIME, min
ELAPSED TIME, min

FIGURE 14